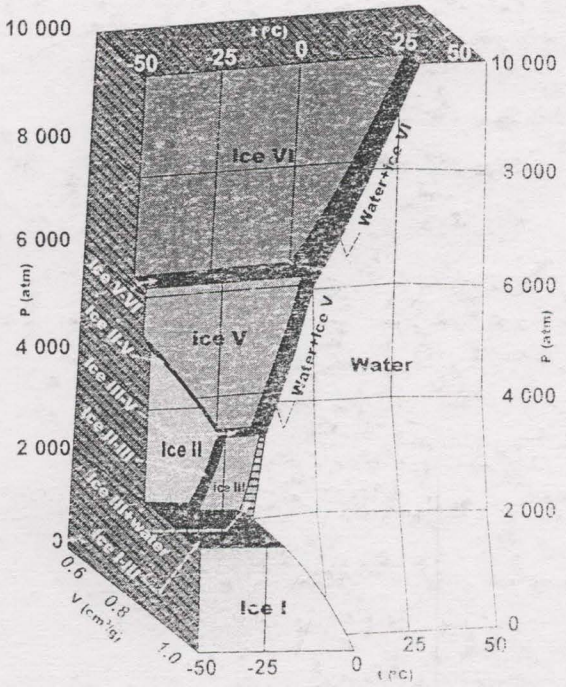
ZOICA CENUŞE

PROBLEMS AND SOLUTIONS IN CHEMICAL THERMODYNAMIC



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INTRODUCTION

Thermodynamics does not change with time; but with experience didactic approaches may become more polished or change and new applications continue to appear.

The fundamental purpose of the book "Introduction in Chemical Thermodynamics" is to present to the students the logical foundations and interrelationships of the theory of thermodynamics, while this book "Problems and Solutions in Chemical Thermodynamics" is to teach the student the methods by which the theoretical methods may be applied to practical problems.

This book provides a study aid and a source of problems for the beginning graduate students in the field of the Chemical Thermodynamics.

The problems are mainly of the classical variety and are presented in the order of difficulty.

Generally speaking, the problems of this book require a usual understanding and "feeling" for Chemical Thermodynamics and, why not, some imagination. In the same time some problems require some understanding of the material beyond the mere "plug the number into the formula" level.

The mathematical and thermodynamical tools that are necessary for this purpose are considered in more detail in the book "Introduction in Chemical Thermodynamics" by Zoica Cenuşe.

It is hoped that the problems of this book will stimulate the students' interest in Chemical Thermodynamics.

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UNITS AND CONVERSION FACTORS

In the study of thermodynamics we can distinguish between variables that are independent of the quantity of matter in a system, the intensive variables, like temperature, pressure, viscosity, concentrations and extensive ones, that depend on the quantity of matter, those values are directly proportional to the quantity of matter like volume, heat capacity, energy, enthalpy, entropy.

To measure these quantities we use units of measurement.

The base units of measurement under the System Internationale d' Units, or SI, are presented in CODATA Bulletin 63, November 1986, "the 1986 Adjustment of the Fundamental Physical Constants" a Report of the CODATA Task Group "publishes by Pergamon Press.

They are presented in table1

Table 1 The 1986 Recommended Values of the Fundamental SI Units

Quantity	Name	Symbol
Length	meter	M
Mass	kilogram	kg
Time	second	s
Electric current	ampere	A
Thermodynamic temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

Same SI – derived units with special names are included in tables 2, 3 and 4.

The standard atmosphere may be used temporarily with SI units, it is defined to be equal to 1.101325×10^5 Pa.

The thermochemical calorie is no longer recommended as a unit of energy, but it is defined in terms of an SI unit as 4.184 J.

The unit of volume is liter (symbol l) and is now defined as 1 dm^3.

In table 4 are presented energy conversion factors.

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Table 2 SI – Derived units

Quantity	Name	Symbol	Expression in terms of other units
Force	newton	N	$m\ kg\ s^{-1}$
Pressure	pascal	Pa	$N\ m^{-2}$
	bar	Bar	$N\ m^{-2}$
Energy, work, quantity of heat	joule	J	N m
Power	watt	W	$J\ s^{-1}$
Electric charge	coulomb	C	A s
Electric potential, electromotive force	volt	V	$W\ A^{-1}$, $J\ C^{-1}$
Celsius temperature	degree celsius	^0C	K
Heat capacity, entropy	joule per kelvin		$J\ K^{-1}$

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Table 3 The 1986 Recommended Values of the Fundamental

Quantity	Symbol	Value	Unit	Relative uncertainty (ppm)
Speed of light in vacuum	c	299792458	$m\ s^{-1}$	(exact)
Permeability of vacuum	μ_0	$4\pi\times10^{-7}$ = 12.566370614	$N\ A^{-2}$	(exact)
Permitivity of vacuum	ε_0	$1/\mu_0c^2$ = 8.854187817	$10^{-7}\ F\ m^{-1}$	(exact)
Newtonian constant of gravitation	G	6.67259(85)	$10^{-11}\ m^3\ kg^{-1}\ s^{-2}$	128
Planck constant	h	6.6260755(40)	10^{-34} J s	0.60
$h/2\pi$	h	1.05457266(63)	10^{-34} J s	0.60
Elementary charge	e	1.60217733(49)	10^{-19} C	0.30
Electron mass	m_e	9.1093897(54)	10^{-31} kg	0.59
Proton mass	m_p	1.6726231(10)	10^{-27} kg	0.59
Proton-electron mass ratio	m_p/m_e	1836.152701(37)		0.020
Fine-structure constant, $\frac{1}{2}\mu_0 ce^2/h$	α	7.29735308(33)	10^{-3}	0.045
Inverse fine-structure constant	α^{-1}	137.0359895(61)		0.045
Rydberg constant, $\frac{1}{2}m_e c\alpha^2/h$	R_∞	10973731.534(13)	m^{-1}	0.0012
Avogadro constant	N_A, L	6.0221367(36)	$10^{23}\ mole^{-1}$	0.59
Faraday constant, $N_A e$	*F*	96485,309(29)	$C\ mole^{-1}$	0.30
Molar gas constant	R	8.314510(70)	$J\ mole^{-1}\ K^{-1}$	8.4
Molar volume (ideal gas)	V_m	22.41410(19)	$l\ mole^{-1}$	8.4
Boltzmann constant R/N_A	k	1.380658(12)	$10^{-23}\ J\ K^{-1}$	8.5
Stefan-Boltzmann constant, $(\pi^2/60)k^4/h^3c^2$	σ	5.67051(19)	$10^{-8} W\ m^{-2}\ K^{-4}$	34
Non-SI units used with SI				
Electron-volt, (e/C) J = $\{e\}$ J	eV	1.60217733(49)	10^{-19} J	0.30
(Unified) atomic mass unit, $1u = m_u = \frac{1}{12}m(^{12}C)$	u	1.6605402(10) 931.49432(28)	10^{-27} kg MeV	0.59 0.30

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Table 4 Energy conversion factors

	Joule	Erg	Thermochemical calorie	International calorie	cm^3 atm	Electron-volt	Kilowatt hour
Joule	1	10^{7}	$2.39006 \cdot 10^{-1}$	$2.38846 \cdot 10^{-1}$	9.86923	$6.24192 \cdot 10^{18}$	$2.7778 \cdot 10^{-7}$
Erg	10^{-7}	1	$2.39006 \cdot 10^{-8}$	$2.38846 \cdot 10^{-8}$	$9.86923 \cdot 10^{-8}$	$6.24192 \cdot 10^{11}$	$2.7778 \cdot 10^{-1}$
Thermochemical calorie	4.18400	$4.184400 \cdot 10^{7}$	1	0.99933	$4.12929 \cdot 10$	$2.61162 \cdot 10^{19}$	1.16222
International calorie	4.18680	$4.18680 \cdot 10^{7}$	1.0067	1	$4.13206 \cdot 10$	$2.31337 \cdot 10^{19}$	$1.16300 \cdot 10$
cm^3 atm	$1.01325 \cdot 10^{-1}$	$1.01325 \cdot 10^{6}$	$2.42173\ 10^{-2}$	$2.42011\ 10^{-2}$	1	$6.32463\ 10^{17}$	$2.81458 \cdot 10$
1 atm	$1.01328 \cdot 10^{-1}$	$1.01328 \cdot 10^{9}$	$2.42180 \cdot 10$	$2.42018 \cdot 10$	$1.00003 \cdot 10^{3}$	$6.32482 \cdot 10^{20}$	$2.81467 \cdot 10$
Electron-volt	$1.620207 \cdot 10^{-19}$	$1.60206 \cdot 10^{-12}$	$3.82904 \cdot 10^{-20}$	$3.82645 \cdot 10^{-20}$	$1.584112 \cdot 10^{-18}$	1	$4.45019 \cdot 10$
Kilowatt hour	$3.6000 \cdot 10^{6}$	$3.6000 \cdot 10^{13}$	$8.60421 \cdot 10^{5}$	$8.5985 \cdot 10^{5}$	$3.55292 \cdot 10^{7}$	$2.24709 \cdot 10^{25}$	1

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1. APPLICATIONS OF THE FIRST LAW OF THERMODYNAMICS

1.1 STATE OF SAMPLE, SYSTEMS AND INDEPENDENT VARIABLES

1.1.1. Calculate the pressure in atmosphere exerted by 2.00 *moles* of chlorobenzene vapor confined to 10.0 liters at 25^0C:(a) using the ideal gas law, and b) using the van der Waals equation: a = 25.43 l^2 *atm* $mole^{-1}$ and b = 0.1453 *l* $mole^{-1}$.

Solution

a) $$P = \frac{nRT}{V} = \frac{2\ mole \times 0.08206\ l\ atm\ mole^{-1}\ K^{-1} \times 298.2\ K}{10.0\ l} = 4.90\ atm$$

b) $$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2} = \frac{2 \times 0.08206 \times 298.2}{10.0 - 2 \times 0.1453} - \frac{2^2 \times 25.43}{10.0^2} = 4.02\ atm$$

1.1.2. The compressibility factor $Z = {}^{PV}/_{nRT}$ for CO_2 at 0^0C and P = 100 *atm* is 0.2007. Calculate the volume occupied by 0.1 *mole* of this gas at 100 *atm* and 0^0C (a) by the ideal gas law, and (b) by making use of the compressibility factor.

Solution

(a) $$V = \frac{nRT}{P} = \frac{0.1\ mole \times 0.08206\ l\ atm\ mole^{-1}\ K^{-1} \times 273.2\ K}{100\ atm} = 22.4 \cdot 10^{-3}\ l$$

(b) $$V = \frac{ZnRT}{P} = \frac{0.2007 \times 0.1 \times 0.08206 \times 273.2}{100} = 4.50 \cdot 10^{-3}\ l$$

1.1.3. The compressibility factor $Z = {}^{PV}/_{nRT}$ for N_2 at -50^0C and 800 *atm* pressure is 1.95, at 100^0C and 200 *atm* it is 1.10. At certain mass of nitrogen occupied a volume of 1.00 *l* at -50^0C and 800 *atm*. Calculate the volume occupied by the same quantity of nitrogen at 100^0C and 200 *atm*.

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Solution

$$V_2 = \frac{P_1 V_1}{P_2} \cdot \frac{Z_2 T_2}{Z_1 T_1} = \frac{800 \times 1.00 \times 1.10 \times 373.2}{200 \times 1.95 \times 223.2} = 3.77\ l$$

1.1.4. The density of gaseous methylamine as a function of pressure at 0^0C is given in table

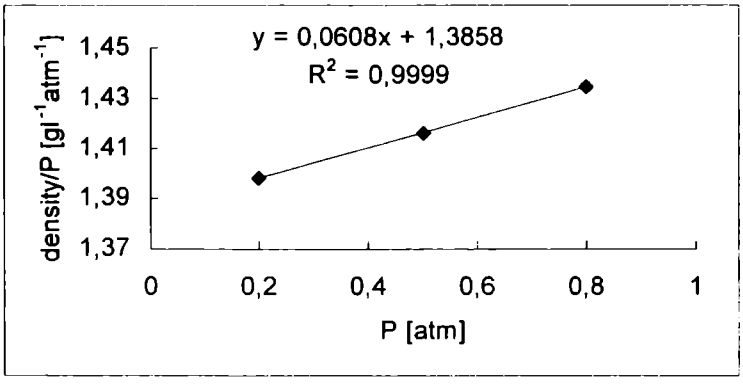
P (*atm*)	0.200	0.500	0.800
$\rho\ (g\ l^{-1})$	0.2796	0.7080	1.1476

Determine the molecular weight of this compound.

Solution

Plot $\left(\rho/P\right)$ versus P and extrapolate at P = 0.

P (*atm*)	0.200	0.500	0.800
$\rho/P\ (g\ l^{-1} atm^{-1})$	1.398	1.416	1.4345



From graph $\lim_{P \to 0}\left(\frac{\rho}{P}\right) = 1.3858$

$$M = \left(\frac{\rho}{P}\right) \cdot RT = 1.3858 \times 0.08206 \times 273.15 = 31.062\ g \cdot mole^{-1}$$

Theoretical for CH_3NH_2 molecular weight is 31.06 $g\ mole^{-1}$.

1.1.5. The coefficient of thermal expansion of helium as a function of pressure is given below. Calculate the temperature in degrees Celsius corresponding to absolute zero.

P [*mm Hg*]	504.8	520.5	760.1	1102.9	1116.5
$\alpha \cdot 10^6\ [K^{-1}]$	3658.9	3660.3	3659.1	3658.2	3658.1

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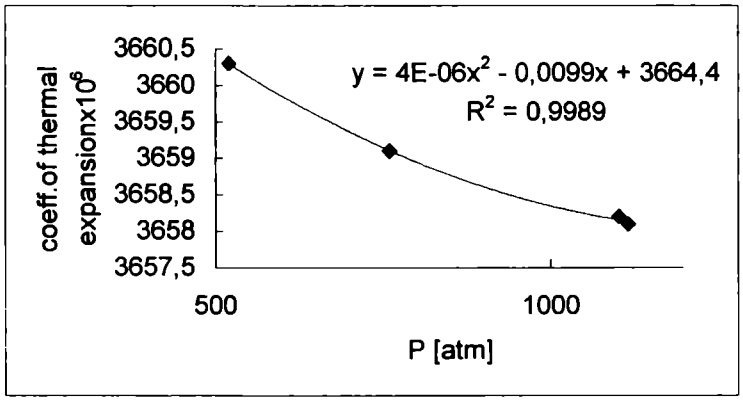
Solution

Plot α versus P



At P = 0 α = $3660.9 \cdot 10^{-6}$ (from graph). Corresponding to Gay Lussac's Law $V_t = V_0 \cdot (1 + \alpha \cdot t)$. When P→0, the behavior of the gas is ideal and Gay Lussac's Law is obeyed. Then, when t = t_0, V_t should be zero and under these conditions:

$$1 + \alpha \cdot t_0 = 0 \Rightarrow t_0 = -\frac{1}{\alpha} = -\frac{1}{3660.9 \cdot 10^{-6}} = -273.16^0 C$$

1.1.6. For a certain hypothetical gas the thermal coefficient of expansion is given by the equation: $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = k_1 \left(\frac{C_P}{C_V}\right) T^{\frac{C_P}{C_V}-1}$ and the coefficient of isothermal compressibility by equation: $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{k_2}{P}$.

What is the equation of state of this gas? Assume that C_P, C_v, k_1 and k_2 are constants.

Solution

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

From α expression:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{k_1 V C_P T^{\frac{C_P}{C_V}-1}}{C_V} \qquad \text{and from } \beta \qquad \left(\frac{\partial V}{\partial P}\right)_T = -\frac{k_2 V}{P}$$

$$\frac{dV}{V} = -k_2 \frac{dP}{P} + k_1 \frac{C_P}{C_V} T^{\frac{C_P}{C_V}-1} dT$$

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$$\ln V = -k_2 \ln P + k_1 \frac{C_P}{C_V} \cdot \frac{T^{\frac{C_P}{C_V}}}{\frac{C_P}{C_V}} + ct \quad \Rightarrow \quad \ln V = -k_2 \ln P + k_1 T^{\frac{C_P}{C_V}} + ct$$

Therefore, the desired equation of state is:

$$P^{k_2} \cdot V = K \cdot e^{k_1 T^{\frac{C_P}{C_V}}}$$

1.1.7. At 0^0C and 1 *atm* the coefficient of thermal expansion of acetone is $1.324 \cdot 10^{-3}$ deg^{-1} and the coefficient of compressibility is $82 \cdot 10^{-6}$ atm^{-1}. Calculate the value of $\left(\partial P / \partial T\right)_V$ for acetone at 0^0C and 1 *atm*. Compare this value with the corresponding derivative of an ideal gas at 0^0C and 1 *atm*.

Solution

$$\alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta = -\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_T \qquad \Rightarrow$$

$$\frac{\alpha}{\beta} = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \left(\frac{\partial P}{\partial T}\right)_V$$

- for acetone: $\left(\frac{\partial P}{\partial T}\right)_V = \frac{1.324 \cdot 10^{-3}}{82 \cdot 10^{-6}} = 16.146\ atm \cdot \deg^{-1}$
- for an ideal gas: $\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{273.16} = 0.00366\ atm \cdot \deg^{-1}$

1.1.8. For a van der Waals gas $V_c = 3b, P_c = a/27b^2$ and $T_c = 8a/27bR$. Evaluate numerically the compressibility factor of a van der Waals gas at the critical point.

Solution

$$Z_c = \frac{P_c V_c}{R T_c} = \frac{a}{27b^2} \cdot \frac{2b}{R} \cdot \frac{27bR}{8a} = \frac{3}{8} = 0.375$$

1.1.9. Evaluate the Boyle temperature of a van der Waals gas in terms of the constants a, b and R.

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Solution

The Boyle temperature of a gas is the temperature at which $\left[\partial(PV)/\partial P\right]_T = 0$ when $P \to 0$. Set up the van der Waals equation in the form:

$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$, multiply by V and set $\left[\partial(PV)/\partial P\right]_T = 0$ at $P \to 0$.

Remember that when P = 0, V = ∞ and

$$PV = nRT \cdot \left(\frac{V}{V - nb}\right) - \frac{n^2 a}{V}$$

$$\left[\frac{\partial(PV)}{\partial P}\right]_T = \left[\frac{nRT}{V - nb} - \frac{nRTV}{(V - nb)^2} + \frac{n^2 a}{V^2}\right] \cdot \left(\frac{\partial V}{\partial P}\right)_T$$

$\left(\partial V/\partial P\right)_T < 0$ under all conditions.

If $\left[\partial(PV)/\partial P\right]_T = 0$, as it should at $P = 0$, T = T_B, than the expression in square brackets equals 0 and hence

$$\frac{nRT}{V - nb} - \frac{nRTV}{(V - nb)^2} + \frac{n^2 a}{V^2} = 0$$

$$nRTV^2 \cdot (V - nb) - nRTV^3 + n^2 a \cdot (V - nb)^2 = 0$$

$$nRT\left[V^3 - nbV^2 - V^3\right] = -n^2 a(V - nb)^2$$

$$n^2 RTbV^2 = n^2 a(V - nb)^2 \quad \Rightarrow \quad RT = \frac{a}{b}\left(1 - \frac{nb}{V}\right)^2$$

At the Boyle point T = T_B, P = 0 and V = ∞, so $RT_B = \frac{a}{b}$ and $T_B = \frac{a}{Rb}$

1.1.10. A certain gas has the equation of state $P = \frac{RT}{V - bT} - \frac{a}{V^3}$, where V represents molar volume and a and b are constants characteristic of the gas. Show that $a = \frac{4RT_c V_c^2}{3}$ and $b = \frac{V_c}{2T_c}$, where V_c and T_c are the critical constants.

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Solution

At critical point:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-bT)^2} + \frac{3a}{V^4} = 0 \quad \Rightarrow \quad \frac{RT_c}{(V_c - bT_c)^2} = \frac{3a}{V_c^4}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT}{(V-bT)^3} - \frac{12a}{V^5} = 0 \quad \Rightarrow \quad \frac{2RT_c}{(V_c - bT_c)^3} = \frac{12a}{V_c^5}$$

Dividing the above equations one can obtain:

$$\frac{2}{V_c - bT_c} = \frac{4}{V_c} \quad \Rightarrow \quad b = \frac{V_c}{2T_c} \quad \Rightarrow \quad a = \frac{RT_c V_c^4}{3(V_c - bT_c)^2} = \frac{4RT_c V_c^2}{3}$$

1.1.11. A hypothetical gas has the equation of state $P = \frac{RT}{V-b} - \frac{a}{V}$ where a and b are constants distinct from zero. Ascertain whether this gas has a critical point. If it has, express the critical constants in terms of a and b. If it has not, explain how you arrive at this conclusion.

Solution

At critical point: $\left(\frac{\partial P}{\partial V}\right)_T = 0$ and $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{a}{V^2} = 0 \quad \Rightarrow \quad \frac{RT}{(V-b)^2} = \frac{a}{V^2}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT}{(V-b)^3} - \frac{2a}{V^3} = 0 \quad \Rightarrow \quad \frac{2RT}{(V-b)^3} = \frac{2a}{V^3}$$

Divide the second equation by the first: $\frac{2}{V-b} = \frac{2}{V}$, from which b = 0. Therefore the two derivatives can never vanish simultaneously unless b = 0, contrary to the stipulation that a and b are distinct from zero, and the gas has no critical point.

1.1.12. For a gas described by van der Waals' equation, $\left(\partial E/\partial V\right)_T = a/V^2$. Obtain an equation that relates the initial and final temperatures to the initial and final volumes in a reversible adiabatic expansion of a van der Waals gas for which $C_V = A + BT$ with A and B constant.

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Solution

$$Q=0, \quad \delta W = dE, \quad PdV = -C_V \mathrm{dT} - \left(\frac{\partial \mathrm{E}}{\partial \mathrm{V}}\right)_{\mathrm{T}} \mathrm{dV}$$

$$\left(\frac{RT}{V-b} - \frac{a}{V^2}\right)dV = -(A+BT)dT - \frac{a}{V^2}dV$$

$$\left(\frac{R}{V-b}\right)dV = -\left(\frac{A}{T}+B\right)dT \quad \Rightarrow \quad R\ln\left[\frac{V_2-b}{V_1-b}\right] = -A\ln\left(\frac{T_2}{T_1}\right) - B(T_2-T_1)$$

1.1.13. Calculate the density in gl^{-1} of air saturated with water vapor at 25^0C. The vapor pressure of water at this temperature is 23.7 *mm Hg*. The composition of dry, CO_2 free air is 78.1 percent N_2, 21.0 percent O_2 and 0.9 percent Ar, by volume.

Solution

$$P_{H_2O} = n_{H_2O} \cdot P \Rightarrow n_{H_2O} = \frac{P_{H_2O}}{P} = \frac{23.7\, mmHg}{760\, mmHg} = 0.03118\, mole$$

$V_{(P=1\ atm)}$ = RT = 0.082 *l atm* $mole^{-1}K^{-1}$ x 298.16 *K* = 24.449 *l atm* $mole^{-1}$. Total number of moles of N_2 + O_2 + Ar remaining in 24.449 liters saturated air = 1-0.3118 = 0.96882. Therefore the total weight of all gases plus water vapor in 24.449 liters of saturated air is:

$$m = m_{N_2} + m_{O_2} + m_{Ar} + m_{H_2O} = (nM)_{N_2} + (nM)_{O_2} + (nM)_{Ar} + (nM)_{H_2O} =$$

$$\left[2\times 14.0067 \times \frac{78.1}{100} \times 0.96882\right]_{N_2} + \left[2\times 15.9994 \times \frac{21.0}{100} \times 0.96882\right]_{O_2} +$$

$$+\left[39.948 \times \frac{0.9}{100} \times 0.96882\right]_{Ar} + \left[18.02 \times 0.03118\right]_{H_2O}$$

$= 21.28 + 6.51 + 0.35 + 0.56 == 28.60\, g$ per 24.47 . The density of water saturated air at 25^0C and 1 *atm* total pressure is therefore $28.60/24.47 = 1.168\, g \cdot l^{-1}$

1.1.14. A certain mixture of helium and argon weighing 5.00 *g* occupies a volume of 10.0 *l* at 25^0C and 1 *atm*. What is the composition of the mixture in weight percent?

Solution

Let G_{Ar} = weight of argon in grams and G_{He} = weight of helium in grams. Then:

$$G_{Ar} + G_{He} = 5.00$$

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Let P = 1.00 *atm* the total pressure, P_{Ar} = partial pressure of argon and P_{He} = partial pressure of helium. Then:

$$P = P_{Ar} + P_{He} = n_{Ar}\frac{RT}{V} + n_{He}\frac{RT}{V} = \frac{G_{Ar}RT}{M_{Ar}V} + \frac{G_{He}RT}{M_{He}V} = \left(\frac{G_{He}}{4} + \frac{5 - G_{He}}{39.9}\right) \times \frac{0.0821 \times 298}{10.0} = 1$$

$$G_{He} = 1.26\ g$$

Weight percent He: $100 \times \frac{1.26}{5.00} = 25.2\,\%$ Weight percent Ar: $100 - 25.2 = 74.8\,\%$

1.1.15. Calculate the vapor pressure of the pure liquid of molecular weight 100 that loses 1.0000 *g* in weight when 0.5000 *mole* of N_2 at 1.00 *atm* is bubbled it at 20.0^0C. Assume that the N_2 is completely saturated with the vapor.

Solution

$$P = \frac{n_x RT}{V} = \frac{n_x RT}{\left(n_x + n_{N_2}\right)\frac{RT}{P_{N_2}}} = \frac{n_x P_{N_2}}{n_x + n_{N_2}} = \frac{\frac{1}{100}}{\frac{1}{100} + 0.500} = 0.0196\ atm = 14.896\ mm\ Hg$$

1.1.16. Orthobaric density data for the compound ethyl mercaptane are given below. ρ_v refers to the saturated vapor. The critical temperature is 225^0C. Using the graph determine the critical density of this substance.

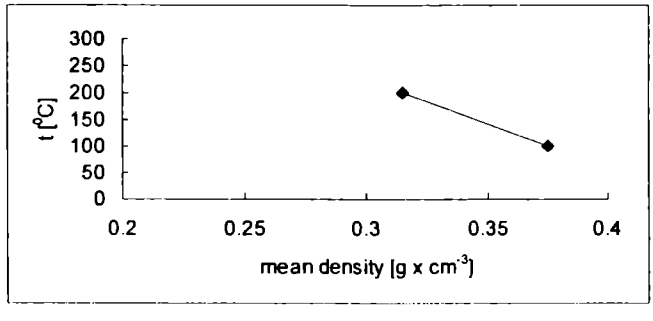
t (^0C)	100.0	200.0
ρ_l ($g\ cm^{-3}$)	0.74	0.53
ρ_v ($g\ cm^{-3}$)	0.01	0.10

Solution

Mean density at 100^0C is: $(0.74 + 0.01)/2 = 0.375$

Mean density at 200^0C is: $(0.53 + 0.01)/2 = 0.315$

Plot the mean densities versus temperature. Draw a straight line through the two points that were plotted.



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The density at which the extrapolation of this line intersects t = 225^0C is the critical density, 0.300 $g\ cm^{-3}$.

1.1.17. For a certain compound (molecular weight, 100) the following data are known. ρ_v is the density of the saturated vapor.

t (^0C)	0.0	20.0	40.0	60.0	80.0	100.0	105.0
ρ_v ($g\ cm^{-3}$)	0.01	0.01	0.01	0.04	0.01	0.026	0.34
ρ_l ($g\ cm^{-3}$)	1.35	1.29	1.23	1.14	1.02	0.80	0.70

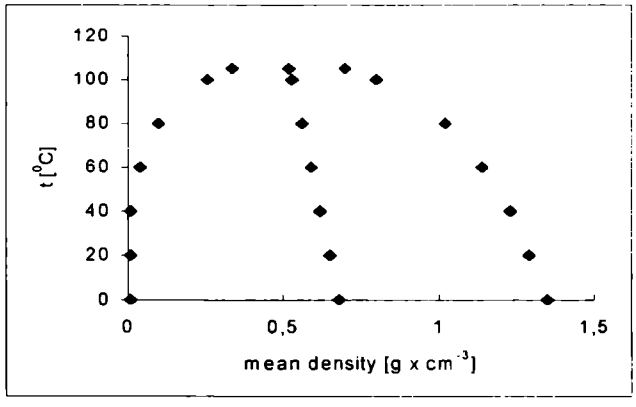
Determine (a) the critical temperature, (b) the critical density, and (c) the critical molar volume.

Solution

The ortobaric densities are: $\frac{1}{2}(\rho_v + \rho_l)$

t (^0C)	0.0	20.0	40.0	60.0	80.0	100.0	105.0
Mean density ($g\ cm^{-3}$)	0.68	0.65	0.62	0.59	0.56	0.53	0.52

Plot both the actual densities and the orthobaric densities versus temperature. Draw a curve through the density points and a straight line through the orthobaric densities.



(a) From the maximum of the curve drawn through the actual density, $t_c = 109^0C$

(b) From the point of intersection between the curve and the straight line, the critical density is 0.51 $g\ cm^{-3}$

(c) The critical volume, in $liter\ mole^{-1}$, is $\frac{100}{0.51 \times 10^3} == 0.196\ l \cdot mole^{-1}$

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1.2. APPLICATIONS OF THE FIRST LAW TO IDEAL AND REAL GASES

1.2.1. Show that for the process of heating an ideal gas

$$\Delta E + (P_2V_2 - P_1V_1) = nC_p(T_2 - T_1)$$

Solution

$$\Delta E + (P_2V_2 - P_1V_1) = \Delta E + (nRT_2 - nRT_1) = \Delta E + nR\cdot(T_2 - T_1) = nC_V\cdot(T_2 - T_1) + nR\cdot(T_2 - T_1) =$$
$$= (nC_V + nR)\cdot(T_2 - T_1) = n\cdot(C_V + R)\cdot(T_2 - T_1) = n\cdot C_P\cdot(T_2 - T_1)$$

1.2.2. From the equation $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ show that $\left(\frac{\partial E}{\partial V}\right)_T = 0$ for a gas that has the equation of state $PV = RT$

Solution

$$PV = RT \quad \Rightarrow \quad PdV + VdP = RdT$$
$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$
$$\left(\frac{\partial E}{\partial V}\right)_T = T\cdot\frac{R}{V} - P = \frac{PV}{V} - P = 0$$

1.2.3. Derive a mathematical expression, involving only constants and readily measurable physical properties, for the work on the surroundings when a gas that has an equation of state $PV = nRT - n^2a/V$ expands reversibly from V_i to V_f at constant temperature.

Solution

$$PV = nRT - \frac{n^2a}{V} \quad \Rightarrow \quad \mathrm{P} = \frac{\mathrm{nRT}}{\mathrm{V}} - \frac{n^2a}{V^2}$$

$$\mathrm{PdV} = \frac{\mathrm{nRTdV}}{\mathrm{V}} - \frac{n^2adV}{V^2} \quad \Rightarrow$$

$$W = -\int_{V_i}^{V_f} PdV = -\int_{V_i}^{V_f}\frac{\mathrm{nRTdV}}{\mathrm{V}} + \int_{V_i}^{V_f}\frac{n^2adV}{V^2} = -nRT\ln\frac{V_f}{V_i} - n^2a\left(\frac{1}{V_f} - \frac{1}{V_i}\right)$$

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1.2.4. Find the work done when 1 *mole* of a gas that has the equation of state $PV = RT + APT - BP$ expands in an isothermal reversible process from volume V_1 to volume V_2. V is molar volume and A and B are constants characteristic of gas.

Solution

$$PV = RT + APT - BP \quad \Rightarrow \quad P \cdot (V - AT + B) = RT \quad \Rightarrow \quad P = \frac{RT}{V - AT + B}$$

$$W = -PdV = -RT \int_{V_1}^{V_2} \frac{dV}{V - AT + B} = -RT \ln\left(\frac{V_2 - AT + B}{V_1 - AT + B}\right)$$

1.2.5. The valve of a cylinder containing initially 10 liters of an ideal gas at 25 *atm* and 25^0C is opened to the atmosphere where the pressure is 760 torr and the temperature is 25^0C. Assuming that the process is isothermal, how much work in liter atmosphere is done on the atmosphere by the action of expanding gas?

Solution

Under normal conditions the heat transfer from the room to the cylinder would not be rapid enough to maintain isothermality, but assuming that the temperature of the expanding gas does remain at 25^0C we proceed as follows. Remembering that the resisting pressure is constant at 1 *atm*

$W = -P_2 \cdot (V_2 - V_1)$ where P_2 is the resisting pressure

$V_1 = 10$ *liters*

$$nRT_1 = P_1V_1 = 25\,atm \times 10\,liters = 250\,l \cdot atm$$

$$V_2 = \frac{nRT_2}{P_2} = \frac{nRT_1}{P_2} = \frac{250\,l \cdot atm}{1.00\,atm} = 250\,l$$

$$W = -1 \times (250 - 10) = -240\,l \cdot atm$$

1.2.6. Calculate the reversible work of compression on 100 *g* of a liquid when the pressure is increased from 10 to 100 *atm* at a constant temperature of 20^0C. The compressibility factor $\beta = 82 \times 10^{-6}\ atm^{-1}$. Assume that β is constant within the pressure range 1 to 100 *atm*, and that the density of the liquid, ρ, at 20^0C and 1 *atm* is 0.792 $g\ cm^{-3}$.

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Solution

For reversible work, $W = -\int PdV$

By definition, $\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

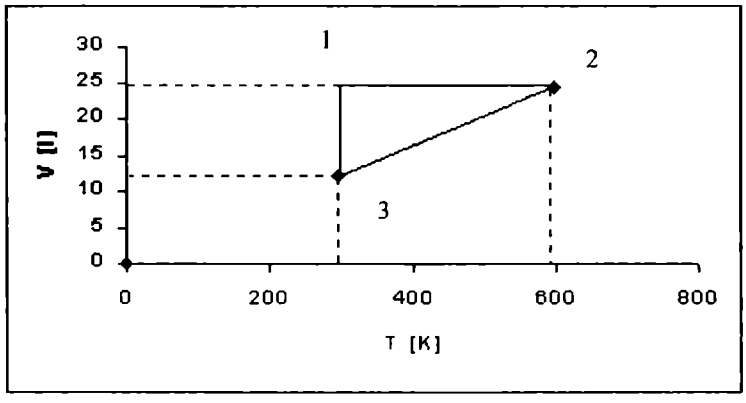
At constant temperature we may write: $dV = -\beta V dP$ and thus

$$W = \int \beta V P dP = \int \beta \frac{m}{\rho} P dP$$

If we take the volume change to be small in the pressure range 1 to 100 *atm*, then:

$$W = \beta \frac{m}{\rho} \int_1^{100} P dP = 82 \cdot 10^{-6} \times \frac{100}{2 \times 0.792} \times \left(100^2 - 10^2\right) = 51.25\, cm^{-3} \cdot atm = 1.242\, cal$$

1.2.7. One mole of monoatomic gas is put through the reversible cycle shown in the figure. Fill in the blank space in the table below:



Stage	P [*atm*]	V [*l*]	T [*K*]
1	1	24.4	298
2	1	24.4	596
3	1	12.2	298

Step	Nature of process	Q [*cal*]	W [*cal*]	ΔE [*cal*]	ΔH [*cal*]
1→2					
2→3					
3→1					
Total cycle					

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Solution

Step 1→2

$$W = \int_{V_1}^{V_2} PdV = 0$$

$$\Delta E = \int_{T_1}^{T_2} nC_V dT = 1 \times \frac{3}{2} R \times (596 - 298) = 889\, cal$$

$$\Delta H = \int_{T_1}^{T_2} nC_P dT = 1 \times \frac{5}{2} R \times (596 - 298) = 1480\, cal$$

$$Q = \Delta E - W = 889 - 0 = 889\, cal$$

Step 2→3

$$W = -\int_{V_2}^{V_3} PdV = -P(V_3 - V_2) = -2 \times (12.2 - 24.4) = 24.4\, l \cdot atm$$

$$W = 24.4\, l \cdot atm \times 24.22\, cal \cdot l^{-1} \cdot atm^{-1} = 591\, cal$$

$$\Delta E = \int_{T_2}^{T_3} nC_V dT = 1 \times \frac{3}{2} R \times (298 - 596) = -889\, cal$$

$$\Delta H = \int_{T_2}^{T_3} nC_p dT = 1 \times \frac{5}{2} R \times (298 - 596) = -1480\, cal$$

$$Q = \Delta E - W = -889 - 591 = -1480\, cal$$

Step 3→1

$$W = \int_{V_3}^{V_1} PdV = nRT \ln \frac{V_1}{V_3} = 1 \times 1.987 \times 298 \times 2.303 \times \lg \frac{12.2}{24.4} = -411\, cal$$

$\Delta E = 0$ (isothermal expansion of an ideal gas)

$\Delta H = 0$ (isothermal expansion of an ideal gas)

$$Q = \Delta E - W = 0 + 411 = 411\, cal$$

Step	Q [*cal*]	W [*cal*]	ΔE [*cal*]	ΔH [*cal*]
1→2	889	0	889	1480
2→3	-1480	591	-889	-1480
3→1	411	-411	0	0
Total cycle	-180	180	0	0

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1.2.8. Calculate the work done on the surroundings when 5 *g* of water are evaporated at 100^0 C and

1 *atm* pressure. The density of water vapor is 5.98 x 10^{-4} *g* cm^{-3} under these conditions. The latent heat of evaporation of water at constant pressure is 540 *cal* g^{-1}. What is the change in internal energy of the system?

Solution

$$H_2O(l) \Leftrightarrow H_2O(g)$$

$$W = -\int_{V_l}^{V_g} PdV = -P \cdot (V_g - V_l) \cong -P \cdot V_g = -P \cdot \frac{m_g}{\rho_g} = -1 \cdot \frac{5}{5.98 \times 10^{-4}} =$$

$$= -0.836 \times 10^4 \; atm \cdot cm^3 = -0.836 \times 0.10134 \times 10^4 \, J = 847.3 \, J$$

$$\Delta H = 5 \times 540 = 2700 \, cal$$

$$\Delta H = \Delta E + P\Delta V = \Delta E + nRT \;\Rightarrow$$

$$\Delta E = \Delta H - nRT = 2700 - \frac{5}{18} \cdot 1.987 \cdot 373.15 = 2494.04 \, cal = 10437.56 \, J$$

1.2.9. Calculate the maximum work performed when one mole of an ideal diatomic gas initially at 0^0 C expands from 1 to 10 liters:

(a) isothermally;

(b) adiabatically.

The answers should be given in joules.

Solution

(a)

$$dW = -PdV \;\Rightarrow$$

$$W_{1,2} = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1} = -1 \cdot 8.31 \cdot 273.15 \cdot \ln \frac{10}{1} = -5226.58 \, J \cdot$$

(c) $$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1} \;\Rightarrow\; T_2 = T_1 \cdot \left(\frac{V_1}{V_2} \right)^{\gamma - 1} = 273.15 \cdot \left(\frac{1}{10} \right)^{0.4} = 108.74 \, K$$

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{7}{2} R}{\frac{5}{2} R} = \frac{7}{5} = 1.4$$

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$$dW = -PdV \quad \text{but} \quad PV^{\gamma} = \text{ct}$$

$$W_{1,2} = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} \frac{ct}{V^{\gamma}} dV = -\frac{ct \cdot V^{-\gamma+1}}{-\gamma+1} = -\frac{PV^{\gamma} \cdot V^{-\gamma+1}}{-\gamma+1} = -\frac{PV}{-\gamma+1} =$$

$$= -\frac{nRT}{-\gamma+1} = -\frac{nR(T_2 - T_1)}{-\gamma+1} = -\frac{1 \cdot 8.31}{1-1.4} \cdot (108.68 - 273.15) = -3415.62\, J$$

1.2.10 One liter of air at 15^0C and at 5 *atm* pressure is heated to 200^0C at constant pressure. It than expands adiabatically until the temperature falls to 100^0C; is than cooled at constant volume to 15^0C and compressed isothermally to its initial state. Calculate the work done by the gas in one cycle assuming air to behave as an ideal diatomic gas.

Solution

Step $1 \rightarrow 2$ P = ct

$$\frac{T_1}{V_1} = \frac{T_2}{V_2} \Rightarrow V_2 = \frac{T_2 V_1}{T_1} = \frac{1 \cdot 473.15}{288.15} = 1.642\, l$$

$$P_1 V_1 = nRT_1 \Rightarrow n = \frac{P_1 V_1}{RT_1} = \frac{1 \cdot 5}{0.08206 \cdot 288.15} = 0.211\, mole$$

$$W_{1,2} = n\int_{V_1}^{V_2} PdV = nP_1 \cdot (V_2 - V_1) = 0.211 \cdot 5 \cdot (1.642 - 1) l \cdot atm = 0.677\, l \cdot atm = 68.34\ \text{J}$$

Step $2 \rightarrow 3$ Q = ct

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1.4$$

$$T \cdot P^{\frac{1-\gamma}{\gamma}} = ct \Rightarrow T_2 \cdot P_2^{\frac{1-\gamma}{\gamma}} = T_3 \cdot P_3^{\frac{1-\gamma}{\gamma}} \Rightarrow P_3^{\frac{1-\gamma}{\gamma}} = \frac{T_2}{T_3} \cdot P_2^{\frac{1-\gamma}{\gamma}} \Rightarrow P_3^{\frac{1-1.4}{1.4}} = \frac{473.15}{373.15} \cdot 5^{\frac{1-1.4}{1.4}} \Rightarrow$$

$$P_3 = 2.178\, atm$$

$$P_2 \cdot V_2^{\gamma} = P_3 \cdot V_3^{\gamma} \Rightarrow V_3^{\gamma} = V_2^{\gamma} \cdot \frac{P_2}{P_3} \Rightarrow V_3^{\gamma} = 1.642 \cdot \frac{5}{2.178} \Rightarrow V_3 = 2.97\, l$$

$$W_{2,3} = \frac{nR}{\gamma - 1}(T_3 - T_2) = \frac{0.211 \times 8.31}{0.4}(-100) = -438.35\, J$$

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Step $3 \rightarrow 4$ $\quad V = ct \quad \Rightarrow \quad \Delta V = ct \quad W_{3,4} = 0$

Step $4 \rightarrow 1$

$$W_{4,1} = -n \cdot \int_{V_4}^{V_1} PdV = -n \cdot \int_{V_4}^{V_1} \frac{RT_4}{V} dV = -nRT_4 \cdot \ln \frac{V_1}{V_4} = -0.211 \times 8.31 \times 288.15 \times \ln \frac{1}{2.97}$$

$$W_{4,1} = 550\,J$$

$$W_{total} = 68.34 - 438.35 + 550 = 180\,J$$

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1.3. JOULE – THOMPSON EFFECT

1.3.1. Starting with $\mu_{JT} = -\left(\frac{1}{C_P}\right)\cdot\left(\frac{\partial H}{\partial P}\right)_T$, derive the formula

$$\mu_{JT} = -\left(\frac{1}{C_P}\right)\cdot\left[\left(\frac{\partial E}{\partial V}\right)_T\cdot\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

Solution

$$H = E + PV;\ \left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial E}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T\cdot\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T$$

$$\mu_{JT} = -\left(\frac{1}{C_P}\right)\cdot\left[\left(\frac{\partial E}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right] = -\left(\frac{1}{C_P}\right)\cdot\left[\left(\frac{\partial E}{\partial V}\right)_T\cdot\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

1.3.2. The Joule-Thompson coefficient of oxygen is + $0.366^0C\ atm^{-1}$. Assuming the coefficient to be independent of temperature under the conditions of this problem, calculate the final temperature of the gas if 10 *moles* of oxygen initially at 20.0 *atm* and 0^0C is allowed to expand adiabatically through a porous plug, as in Joule-Thompson experiment, until the final pressure is 1.0 *atm*.

Solution

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = +0.366 \quad \Rightarrow \quad dT = 0.366 dP \quad \Rightarrow \quad T_2 - T_1 = 0.366\cdot(1-20) = -6.96$$

Since $\mu_{JT} > 0$, the expanded gas is colder than it was initially and the final temperature is - 6.96^0C.

1.3.3. Evaluate the Joule-Thompson coefficient $\mu_{JT} = \frac{1}{C_P}\cdot\left[T\cdot\left(\frac{\partial V}{\partial T}\right)_P - V\right] = \left(\frac{\partial T}{\partial P}\right)_H$ in terms of a, R, T, and C_P for a gas that has the equation of state $V = \frac{nRT}{P} - \frac{na}{R^2T^2}$. Would the gas have an inversion temperature? Explain.

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Solution

$V = \frac{nRT}{P} - \frac{na}{R^2T^2} \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} + \frac{2na}{R^2T^3}$ Substituting this relation in μ_{JT} we obtain

$$\mu_{JT} = \frac{1}{C_P} \cdot \left[T \cdot \frac{nR}{P} + \frac{2na}{R^2T^2} - \frac{nRT}{P} + \frac{na}{R^2T^2} \right] = \frac{3na}{C_P R^2 T^2}$$

At the inversion temperature, $\mu_{JT} = 0$. This could happen only if $C_P = \infty$, $T = \infty$ or $a = 0$. Thus this gas does not have an inversion temperature.

1.3.4. The Joule-Thompson coefficient of a van der Waals gas is given by the equation: $\mu_{JT} = \frac{1}{C_P} \cdot \left(\frac{2a}{RT} - b - \frac{3abP}{R^2T^2} \right)$. Derive an expression for the inversion temperature as a function of pressure.

Solution

At the inversion temperature T_i, $\mu_{JT} = 0$; hence

$$\frac{2a}{RT} - b - \frac{3abP}{R^2T^2} = 0 \Rightarrow bR^2T_i^2 - 2aRT_i^2 + 3abP = 0$$

This is a quadratic equation. Solving for T_i, we obtain:

$$T_i = \frac{2aR \pm \sqrt{4a^2R^2 - 12ab^2R^2P}}{2bR^2} = \frac{a \pm \sqrt{a^2 - 3ab^2P}}{bR}$$

Since we are dealing with a quadratic equation, we have two values for inversion temperature corresponding to any given pressure. Real gases do in fact have two inversion temperatures at any given pressure.

1.3.5. For a gas the equation of state $P(V - nb) = nRT$ and $\left(\frac{\partial E}{\partial V}\right)_T = 0$. For this gas derive an expression involving only constants (such as b and R) and readily measurable physical properties (such as P or V, and n, T, C_P and C_V) for:

(a) The coefficient of thermal expansion, α, where $\alpha = \left(\frac{1}{V}\right) \cdot \left(\frac{\partial V}{\partial T}\right)_P$.

(b) The work done upon the surroundings by the gas during its isothermal reversible expansion from V_i to V_f.

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(c) The function of T and V for the reversible adiabatic expansion analogous to the ideal gas formula $\frac{T_1}{T_2}=\left(\frac{V_2}{V_1}\right)^{\gamma-1}$, where $\gamma=\frac{C_P}{C_V}$. Assume that C_P and C_V are constant.

(d) The Joule-Thompson coefficient,

$$\mu_{JT}=\frac{1}{C_P}\cdot\left[T\cdot\left(\frac{\partial V}{\partial T}\right)_P-V\right]=\left(\frac{\partial T}{\partial P}\right)_H$$

Solution

(a) $V=\frac{nRT}{P}+nb; \qquad \left(\frac{\partial V}{\partial T}\right)=\frac{nR}{P} \qquad \alpha=\frac{\mathrm{nR}}{\mathrm{PV}}$

We cannot substitute nRT for PV in the last equation to get $\alpha = 1/T$ here because this gas is not ideal

(b) $P=\frac{nRT}{V-nb}; \quad \Rightarrow \quad PdV=\frac{nRTdV}{V-nb}$

$W=-\int_{V_i}^{V_f}PdV=-\int_{V_i}^{V_f}\frac{nRT}{V-nb}dV$ Integrating with the assumption that T is constant:

$$W=-nRT\ln\left[\frac{V_f-nb}{V_i-nb}\right]$$

(c) $Q=0$ (adiabatic), so $\Delta E=Q+W=0+W=W$

Since $\Delta E=W$, then $nC_vdT=PdV$, since $\left(\partial E/\partial V\right)_T=0$

$nC_VdT=-\frac{nRTdV}{V-nb} \quad \Rightarrow \quad \mathrm{nC_V}\frac{\mathrm{dT}}{\mathrm{T}}=-\frac{nRdV}{V-nb}$

On integration $\Rightarrow \quad C_V\ln\left(\frac{T_2}{T_1}\right)=-R\ln\left[\frac{(V_2-nb)}{(V_1-nb)}\right]$

Or $\Rightarrow \quad \left(\frac{T_2}{T_1}\right)^{C_V}=\left[\frac{(V_2-nb)}{(V_1-nb)}\right]^{-R}$ or $\left(\frac{T_2}{T_1}\right)=\left[\frac{(V_2-nb)}{(V_1-nb)}\right]^{-R/C_V}$

We cannot substitute (C_P-C_V) for R in the exponent R/C_V because this gas is not ideal and $(C_P-C_V)=R$ only for an ideal gas.

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(d) $$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \Rightarrow \mu_{JT} = \frac{1}{C_P}\cdot\left[T\cdot\frac{nR}{P} - V\right] = \frac{1}{C_P}\cdot\left[\frac{(V-nb)P}{P} - V\right] = -\frac{nb}{C_P}$$

1.3.6. The value of Joule-Thompson coefficient for NH_3 at 300^0C and 40 *atm* is 0.370 *deg* atm^{-1}. Compare the experimental value with the calculated one:

(a) from data P – V – T

t (^0C)	225	250	275	300	325
V ($cm^3\ mole^{-1}$)	962	1017	1076	1136	1186

(b) using van der Waals equation;

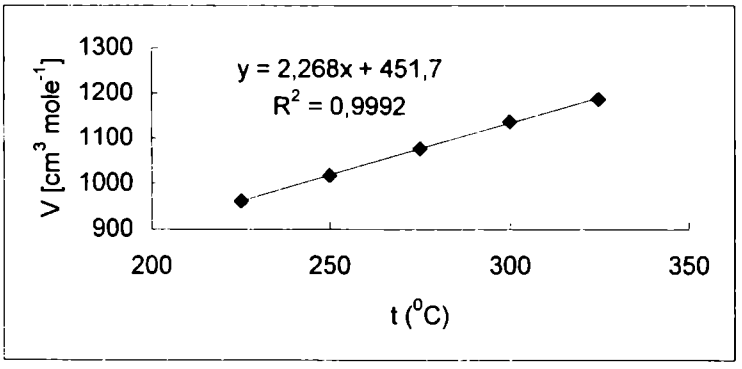
(c) calculate the inversion temperature.

The molar heat capacity of NH_3 is 11.0 *cal* mol^{-1} deg^{-1}. The van der Waals constants for NH_3 are: a = 4.18 l^2 *atm* $mole^{-2}$ and b = 0.0373 *l* $mole^{-1}$

Solution

(a) We already know that: $$\mu_{JT} = \frac{T\cdot\left(\frac{\partial V}{\partial T}\right)_P - V}{C_P}$$

From the graphical representation of volume versus temperature we obtain that:



$$\left(\frac{\partial V}{\partial T}\right)_P = 2.268\,cm^3\ \text{deg}^{-1}\ mole^{-1}$$

$$\mu_{JT} = \frac{573.15\times 2.268 - 1136}{11} = 14.90\,cm^3 cal^{-1}\ \text{deg}$$

While $R = 1.987\ cal\ mol^{-1}\ \text{deg}^{-1} = 0.08206\ l\ atm\ mole^{-1}\ \text{deg}^{-1}$

$$1\,cal = 41.26\,cm^3 atm \Rightarrow \mu_{JT} = 14.90\,cm^3 cal^{-1}\ \text{deg} = \frac{14.90}{41.26} = 0.361\,\text{deg}\,atm^{-1}$$

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(b) $\mu_{JT} = \dfrac{T\cdot\left(\dfrac{\partial V}{\partial T}\right)_P - V}{C_P}$ and $\left(P+\dfrac{a}{V^2}\right)\cdot(V-b)=RT$

$PV - Pb + \dfrac{a}{V} - \dfrac{ab}{V^2} = RT$ derive with respect V and T at constant pressure we obtain :

$$PdV - \frac{a}{V^2}dV + \frac{2ab}{V^3}dV = RdT \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P - \frac{a}{V^2} + \frac{2ab}{V^3}} = \frac{RT}{T\cdot\left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right)} =$$

$$\frac{\left(P+\frac{a}{V^2}\right)\cdot(V-b)}{T\cdot\left(P - \frac{a}{V^2} + \frac{2ab}{V^3}\right)}\cdot\frac{V}{V} = \frac{V}{T}\cdot\frac{PV - Pb + \frac{a}{V} - \frac{ab}{V^2}}{PV - \frac{a}{V} + \frac{2ab}{V^2}} = \frac{V}{T}\cdot\frac{PV - \frac{a}{V} + \frac{2ab}{V^2} + \frac{2a}{V} - \frac{3ab}{V^2} - Pb}{PV - \frac{a}{V} + \frac{2ab}{V^2}} =$$

$$\frac{V}{T}\cdot\left[1 + \frac{\frac{2a}{V} - \frac{3ab}{V^2} - Pb}{PV - \frac{a}{V} + \frac{2ab}{V^2}}\right] \cong \frac{V}{T}\cdot\left[1 + \frac{\frac{2a}{V} - \frac{3ab}{V^2} - Pb}{PV}\right] = \frac{V}{T}\cdot\left[1 + \frac{2a}{PV^2} - \frac{3ab}{PV^3} - \frac{b}{V}\right] = \frac{V-b}{T} + \frac{2a}{PVT} - \frac{3ab}{PTV^2}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V-b}{T} + \frac{2a}{PVT} - \frac{3ab}{PVTV} = \frac{V-b}{T} + \frac{2a}{RT^2} - \frac{3abP}{R^2T^3}$$

$$\mu_{JT} = \frac{T\cdot\left(\frac{\partial V}{\partial T}\right)_P - V}{C_P} = \frac{\frac{2a}{RT} - \frac{3abP}{R^2T^2} - b}{C_P} = \frac{\frac{2\times4.18}{0.082\times573.15} - \frac{3\times4.18\times0.0373\times40}{0.082^2\times573.15^2} - 0.0373}{11\times0.04126} = 0.291\,\text{deg}\,atm^{-1}$$

The value of μ_{JT} calculated with van der Waals equation are not in good agreement with the experimental value because the van der Waals equation does not apply at high pressure.

(c) The inversion temperature Ti can be obtain for $\mu_{JT} = 0$. We obtain a quadratic equation with the roots:

$$\frac{2a}{RT} - b - \frac{3abP}{R^2T^2} = 0 \Rightarrow bR^2T_i^2 - 2aRT_i + 3abP = 0$$

$$T_i = \frac{2aR \pm \sqrt{4a^2R^2 - 12ab^2R^2P}}{2bR^2} = \frac{a \pm \sqrt{a^2 - 3ab^2P}}{bR}$$

$$T_i = \frac{4.18 \pm \sqrt{4.18^2 - 3\times4.18\times0.0373^2\times40}}{0.0373\times0.082} = \frac{4.18 \pm 4.0956}{0.0030586}$$

$T_1 = 2705.68\ K$ and $T_2 = 27.59\ K$

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1.3.7. The volume V of liquid water at t^0C and 1 *atm* is related to volume V_0 at at 0^0C and 1 *atm* by: $V = V_0 \cdot \left(1 - 6.427 \times 10^{-5} \cdot t + 8.5053 \times 10^{-6} \cdot t^2 - 6.7900 \times 10^{-8} \cdot t^3\right)$

This expression is valid from 0 to 33^0C. The compressibility of water near 0^0C and 1 *atm* is 5.25×10^{-5} atm^{-1}. Find the internal pressure $\left(\partial E / \partial V\right)_T$ of liquid water at 1.00^0C and 1.00 *atm*. Indicate and explain any noteworthy difference between this result and the internal pressure of most liquids.

Solution

$$\left(\frac{\partial E}{\partial V}\right)_T = T \cdot \left(\frac{\partial P}{\partial T}\right)_V - P = -T \cdot \frac{\left(\partial V / \partial T\right)_P}{\left(\partial V / \partial P\right)_T} - P$$

$$\left(\frac{\partial V}{\partial T}\right)_P = V_0 \cdot \left(6.427 \times 10^{-5} + 2 \times 8.5053 \times 10^{-6} \cdot t - 3 \times 6.7900 \times 10^{-8} \cdot t^2\right) = -4.746 \times 10^{-5} \cdot V_0$$

$$\left(\frac{\partial V}{\partial P}\right)_T = -5.25 \times 10^{-5} \cdot V_0$$

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{-274 \cdot \left(-4.746 \times 10^{-5} \cdot V_0\right)}{-5.25 \times 10^{-5} \cdot V_0} - 1.00 = -249 \ atm$$

Usually $\left(\partial E / \partial V\right)_T$ for a liquid or solid is large and positive signifying that the energy decreases on compression. Here, however, the energy increases on compression because a decrease in volume can occur only at the expense of some of the hydrogen bonds, which impose a rather open structure on water.

1.3.8. For a certain substance, $\left(\partial H / \partial P\right)_T = 0$ and $\left(\partial E / \partial V\right)_T = 0$

(a) Show that this substance is an ideal gas (that is, has the equation of state $PV = kT$, where k is a constant).

(b) Ascertain whether either of these equations taken alone suffices to imply that the substance is an ideal gas.

Solution

(a) $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P = 0$

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$$\frac{T}{V}\cdot\left(\frac{\partial V}{\partial T}\right)_P = 1 \qquad \Rightarrow \qquad \left(\frac{\partial \ln V}{\partial \ln T}\right)_P = 1$$

$\ln V = \ln T + \ln f(P)$, where $f(P)$ is an arbitrary function of P $\Rightarrow V = T\cdot f(P)$ (1)

$$\left(\frac{\partial E}{\partial V}\right)_T = T\cdot\left(\frac{\partial P}{\partial T}\right)_V - P = 0$$

$$\frac{T}{P}\cdot\left(\frac{\partial P}{\partial T}\right)_V = 1 \qquad \Rightarrow \qquad \left(\frac{\partial \ln P}{\partial \ln T}\right)_V = 1$$

$\ln P = \ln T + \ln g(V)$, where $g(V)$ is an arbitrary function of V $\Rightarrow P = T\cdot g(V)$ (2)

Comparing (1) and (2), we see that:

$$T = \frac{V}{f(P)} = \frac{P}{g(V)}, \text{ or } P\cdot f(P) = V\cdot g(V)$$

The left side depends only on P and the right side only on V; therefore both sides must be constant:

$$P\cdot f(P) = V\cdot g(V) = k;\quad f(P) = \frac{k}{P};\quad g(V) = \frac{k}{V}. \qquad \text{Thus } T = \frac{PV}{k} \text{ or } PV = kT$$

(b) Equation (1) alone, requires only that V be proportional to T; it leaves unspecified the dependence of V on P. Similarly, equation (2) alone makes P proportional to T but falls to fit the dependence of P on V. Thus neither equation alone implies that the substance is an ideal gas. For example, $P = \frac{nRT}{V - nb}$ is an instance of equation (2) but describes a non-ideal gas.

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1.4. HEAT CAPACITIES

1.4.1. Prove that for any substance: $C_P - C_V = \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \cdot \left(\frac{\partial V}{\partial T}\right)_P$

Solution

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V = \left[\frac{\partial (E + PV)}{\partial T}\right]_P - \left(\frac{\partial E}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_P + P \cdot \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V$$

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \Rightarrow \left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P + P \cdot \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V = \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \cdot \left(\frac{\partial V}{\partial T}\right)_P$$

1.4.2. Prove that $C_P - C_V = \frac{\alpha^2 \cdot T \cdot V}{\beta}$ and then calculate the difference $(C_P - C_V)$ for 1 *mole* of water at $20^0 C$. At that temperature, the coefficient of compressibility is $49 \times 10^{-6}\ atm^{-1}$ and the coefficient of thermal expansion is $2.1 \times 10^{-4}\ deg^{-1}$.

Solution

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV \Rightarrow \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_V}{T} + \left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P \Rightarrow$$

$$\frac{C_P}{T} = \frac{C_V}{T} + \left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P \Rightarrow C_P - C_V = T \cdot \left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P$$

But

$$\left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_V \cdot \left(\frac{\partial P}{\partial V}\right)_T = -1 \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial P}{\partial V}\right)_T \Rightarrow C_P - C_V = -T \cdot \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$$

We know that:

$$\alpha = \frac{1}{V} \cdot \left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \alpha \cdot V \text{ and } \beta = -\frac{1}{V} \cdot \left(\frac{\partial V}{\partial P}\right)_T \Rightarrow \left(\frac{\partial V}{\partial P}\right)_T = -\beta \cdot V$$

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$$C_P - C_V = -T \cdot \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T = -T \cdot \alpha^2 \cdot V^2 \cdot \left(-\frac{1}{\beta \cdot V}\right) = \frac{\alpha^2 \cdot T \cdot V}{\beta}$$

$$C_P - C_V = \frac{\alpha^2 \cdot T \cdot V}{\beta} = \frac{\left(2.1 \times 10^{-4}\right)^2 \cdot 293.15 \cdot \dfrac{0.082 \times 293.16}{1}}{49 \times 10^{-6}} = 6.34\, l\, atm\, \text{deg}^{-1} = 153.67\, cal\, \text{deg}^{-1}$$

1.4.3. Show that each of the formulas listed below simplifies $C_P - C_V = R$ for the special case of an ideal gas.

(a) $$C_P - C_V = \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \cdot \left(\frac{\partial V}{\partial T}\right)_P$$

(b) $$C_P - C_V = -\frac{T \cdot \left(\dfrac{\partial V}{\partial T}\right)_P^2}{\left(\dfrac{\partial V}{\partial P}\right)_T}$$

(c) $$C_P - C_V = \frac{\alpha^2 \cdot T \cdot V}{\beta}$$

where $\alpha = \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$ and $\beta = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$

Solution

(a) For an ideal gas, $\left(\dfrac{\partial E}{\partial V}\right)_T = 0$ and $PV = RT \Rightarrow \left(\dfrac{\partial V}{\partial T}\right)_P = \dfrac{R}{P}$

Substituting in the formula (a) $\Rightarrow C_P - C_V = P \cdot \left(\dfrac{\partial V}{\partial T}\right)_P = P \cdot \dfrac{R}{P} = R$

(b) $$V = \frac{RT}{P} \Rightarrow \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2} \quad \Rightarrow \quad C_P - C_V = -\frac{T \cdot \left(\dfrac{\partial V}{\partial T}\right)_P^2}{\left(\dfrac{\partial V}{\partial P}\right)_T} = -\frac{T \cdot \dfrac{R^2}{P^2}}{-\dfrac{RT}{P^2}} = R$$

(c) Using $\left(\dfrac{\partial V}{\partial T}\right)_P$ and $\left(\dfrac{\partial V}{\partial P}\right)_T$ as evaluated in (a) and (b),

$$\alpha = \frac{1}{V} \cdot \frac{R}{P} = \frac{1}{T} \quad \text{and} \quad \beta = \left(-\frac{1}{V}\right) \cdot \left(-\frac{RT}{P^2}\right) = \frac{1}{P}$$

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$$C_P - C_V = \frac{T \cdot V \cdot \frac{1}{T^2}}{\frac{1}{P}} = \frac{PV}{T} = R$$

1.4.4. An imaginary gas has the equation of state $PV^2 = n^2 KT$ (where K is a constant), and its heat capacity C_V is independent of temperature and pressure. For this gas E depends only on T, as for an ideal gas.

(a) Obtain an equation that relates the initial and final pressures to the initial and final temperatures in a reversible adiabatic expansion of this gas.

(b) Find $C_P - C_V$ for this gas in terms of T, P and K.

Solution

(a) $\delta Q = 0 \quad dE = -\delta W \quad nC_V dT = -PdV$

From the equation of state $\Rightarrow$

$$P = \frac{n^2 KT}{V^2} \Rightarrow nC_V dT = -\frac{n^2 KT}{V^2} dV \Rightarrow \frac{nC_V dT}{T} = -\frac{n^2 K}{V^2} dV$$ Integrating we obtain:

$$nC_V \ln\left(\frac{T_2}{T_1}\right) = n^2 K\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

(b) $$C_P - C_V = \left[P + \left(\frac{\partial E}{\partial V}\right)_T\right] \cdot \left(\frac{\partial V}{\partial T}\right)_P = P \cdot \left(\frac{\partial V}{\partial T}\right)_P$$ because $\left(\frac{\partial E}{\partial V}\right)_T = 0$

$$PV^2 = n^2 KT \Rightarrow V^2 = \frac{n^2 KT}{P} \Rightarrow V = n \cdot \left(\frac{KT}{P}\right)^{1/2} \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{2} \cdot n \cdot \left(\frac{K}{PT}\right)^{1/2}$$

$$C_P - C_V = P \cdot \left(\frac{\partial V}{\partial T}\right)_P = P \cdot \frac{1}{2} \cdot n \cdot \left(\frac{K}{PT}\right)^{1/2} = \frac{1}{2} \cdot n \cdot \left(\frac{KP}{T}\right)^{1/2}$$

1.4.5. Show that: $\left(\frac{\partial C_P}{\partial P}\right)_T = -\mu_{JT} \cdot \left(\frac{\partial C_P}{\partial T}\right)_P - C_P \cdot \left(\frac{\partial \mu_{JT}}{\partial T}\right)_P$

Solution

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \left[\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial T}\right)_P\right]_T = \frac{\partial^2 H}{\partial P \partial T} = \left[\frac{\partial}{\partial T}\left(\frac{\partial H}{\partial P}\right)_T\right]_P$$

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$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \Rightarrow 0 = \left(\frac{\partial H}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T \cdot \left(\frac{\partial P}{\partial T}\right)_H$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_H = -C_P \cdot \mu_{JT}$$

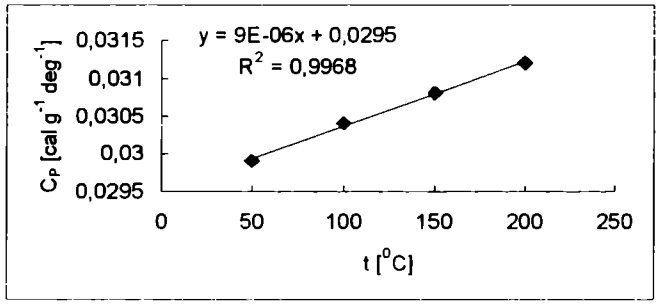
$$\left(\frac{\partial C_P}{\partial P}\right)_T = \left[\frac{\partial}{\partial T}\left(-C_P \cdot \mu_{JT}\right)\right]_P = -\mu_{JT} \cdot \left(\frac{\partial C_P}{\partial T}\right)_P - C_P \cdot \left(\frac{\partial \mu_{JT}}{\partial T}\right)_P$$

1.4.6. Find an expression for the relation between the true heat capacity and the increment of the enthalpy of a mole of lead at temperatures of 50 to 200^0C, at which the mean specific heat capacities of lead have the following values:

t (^0C)	50	100	150	200
C_P ($cal\ g^{-1}\ deg^{-1}$)	0.0299	0.0304	0.0308	0.0312

Solution

Using the method of least squares, let us find the coefficients of the equation $C_P = a + bt$



As we can see from the graphical representation a = 0.0295 and b = 9×10^{-6}

Consequently $C_P = 0.0295 + 9\times10^{-6}t$

From Kirrchoff's Law:

$$\Delta H_t^0 = \Delta H_{25}^0 + M_{Pb} \cdot \int_{25}^{t} C_P dt \Rightarrow \Delta H_T^0 - \Delta H_{25}^0 = M_{Pb} \cdot \int_{25}^{t} C_P dt \Rightarrow$$

$$\Delta H_t^0 - \Delta H_{25}^0 = 207.19 \cdot \int_{25}^{t} \left(0.0295 + 9\times10^{-6}t\right)dt \Rightarrow$$

$$\Delta H_t^0 - \Delta H_{25}^0 = 207.19 \cdot 0.0295 \cdot (t - 25) + \frac{207.19 \cdot 9\times10^{-6}}{2} \cdot \left(t^2 - 25^2\right)$$

$$\Delta H_t^0 - \Delta H_{25}^0 = 9.32\times10^{-4} \cdot t^2 + 6.112 \cdot t - 153.38$$

The values of $\Delta H_t^0 - \Delta H_{25}^0$ for the temperatures indicated in the table are:

t (^0C)	50	100	150	200
$\Delta H_t^0 - \Delta H_{25}^0$ ($cal\ mole^{-1}$)	154.55	467.14	784.39	1106.3

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1.5. PARTIAL MOLAR QUANTITIES

1.5.1. For the system H_2O – NaCl we have

$$V_{tot} = 55.51 \cdot V_{H_2O} + 16.4 \cdot m + 2.5 \cdot m^2 - 1.2 \cdot m^3$$

where $V_{H_2O} = V_1^0 = 18.069\, cm^3\ mole^{-1}$ represents the molar volume of pure water and m is the molality of the solution. Find the partial and apparent molar volumes of sodium chloride in its half-molal aqueous solution.

Solution

$$\overline{V}_2 = \overline{V}_{NaCl} = \left(\frac{\partial V_{tot}}{\partial n_2}\right)_{T,P,n_1} = \left(\frac{\partial V_{tot}}{\partial m}\right)_{T,P,n_1} \Rightarrow \overline{V}_{NaCl} = 16.4 + 5 \cdot m - 3.6 \cdot m^2$$

For m = 0.5

$$\overline{V}_{NaCl} = 16.4 + 5 \cdot 0.5 - 3.6 \cdot 0.5^2 = 18.0\ cm^3\ mole^{-1}$$

$$V_{tot} = 1000 + 16.4 \cdot 0.5 + 2.5 \cdot 0.25 - 1.2 \cdot 0.125 = 1008.675\, cm^3\ mole^{-1}$$

$$^{\phi}V_2 = \phi_2 = \frac{V - n_1 \cdot V_1^0}{n_2} = \frac{V - n_1 \cdot V_1^0}{m} = \frac{1008.675 - 1000}{0.5} = 17.35\, cm^3\ mole^{-1}$$

1.5.2. The density of an aqueous alcohol solution containing 60% CH_3OH is 0.8946 $g\ cm^{-3}$, and the partial molar volume of the water in it is 16.8 $cm^3\ mole^{-1}$. Find the partial molar volume of the alcohol in this solution.

Solution

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{\frac{m_2}{M_2}}{\frac{m_1}{M_1} + \frac{m_2}{M_2}} = \frac{\frac{60}{32}}{\frac{40}{18} + \frac{60}{32}} = 0.4576 \Rightarrow x_1 = 1 - x_2 = 0.5424$$

$$V = \frac{\overline{M}}{\rho} = \frac{x_1 \cdot M_1 + x_2 \cdot M_2}{\rho} = \frac{0.5424 \times 18 + 0.4576 \times 32}{0.8946} = 27.3\, cm^3\ mole^{-1}$$

$$\overline{V}_2 = \frac{V - x_1 \cdot \overline{V}_1}{x_2} = \frac{27.3 - 0.5426 \times 16.8}{0.4576} = 39.75\, cm^3\ mole^{-1}$$

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1.5.3. For the solute (2) in dilute solutions in a certain solvent, the partial molal volume is given by the equation $\bar{V}_2 = a + b \cdot m$, where m is the molality of the solute and a, b are constants. Express the partial molal volume $\bar{V}_1$ in terms of a, b, m and quantities characteristic of the solvent.

Solution

$\bar{V}_2 = a + b \cdot m \Rightarrow d\bar{V}_2 = b \cdot dm$

$n_1 d\bar{V}_1 + n_2 d\bar{V}_2 = 0; \quad n_1 = \dfrac{1000}{M_1}; \quad n_2 = m$ (M_1 = molecular weight of solvent)

$$d\bar{V}_1 = -\frac{n_2}{n_1} \cdot d\bar{V}_2 = -\frac{m \cdot M_1 \cdot b \cdot dm}{1000} \Rightarrow \bar{V}_1 = -\frac{m^2 \cdot M_1 \cdot b}{2000} + C$$ (C = integration constant)

When $m = 0$, $\bar{V}_1 = V_1^0 = C \Rightarrow \bar{V}_1 = V_1^0 - \dfrac{m^2 \cdot M_1 \cdot b}{2000}$

(V_1^0 = molar volume of pure solvent)

1.5.4. Let a mixture of two gases, X and Y, have the equation of state

$$\frac{PV}{RT} = (n_x + n_y) \cdot (1 + \beta P) + \alpha \cdot (n_x n_y)^{1/2} P$$

where α and β may depend on T, but not on P, n_x or n_y.

(a) Find the partial molar volume $\bar{V}_x$ in terms of P, T, α, β, n_x, n_y and R.

(b) Find $\Delta G_x = \int_{P_1}^{P_2} \bar{V}_x \, dP$ for an isothermal expansion of the gas mixture from P_1 to P_2.

Solution

(a) $$V = RT\left[\left(\frac{n_x + n_y}{P}\right) + \beta \cdot (n_x + n_y) + \alpha \cdot (n_x n_y)^{1/2}\right]$$

$$\bar{V}_x = \left(\frac{\partial V}{\partial n_x}\right)_{T,P,n_y} = RT\left[\frac{1}{P} + \beta + \frac{1}{2} \cdot \alpha \cdot \left(\frac{n_y}{n_x}\right)^{1/2}\right]$$

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(b) $\Delta G_x = \int_{P_1}^{P_2} \overline{V}_x dP = RT\left[\ln\frac{P_2}{P_1} + \left(\beta + \frac{1}{2}\cdot\alpha\cdot\left(\frac{n_y}{n_x}\right)^{1/2}\right)\cdot(P_2 - P_1)\right]$

1.5.5. (a) A solution contains n_1 moles of component 1 and n_2 moles of component 2. Their molecular weights are M_1 and M_2, respectively. Obtain an expression for the partial molar volume $\overline{V}_2$ of component 2 in terms of n_1, n_2, the density ρ of the solution, the derivatives of ρ with respect to n_2, at constant n_1, and the molecular weights.

(b) Let x_1 and x_2 be the mole fractions of 1 and 2 in the solution. Show that:

$$\overline{V}_2 = \frac{M_2}{\rho} - (M_1 x_1 + M_2 x_2)\cdot\frac{x_1}{\rho^2}\cdot\frac{d\rho}{dx_2}$$

(c) The density in $g\ cm^{-3}$ of a water – methanol (CH_3OH) solution at 25^0C is given by the equation:

$$\rho = 0.9971 - 0.28930\cdot x_2 + 0.29907\cdot x_2^2 - 0.60876\cdot x_2^3 + 0.59438\cdot x_2^4 - 0.20581\cdot x_2^5$$

where x_2 is the mole fraction of methanol. Calculate $\overline{V}_2$ in a water – methanol solution at 25^0C with $x_2 = 0.100$.

Solution

(a) $$V = \frac{M_1 n_1 + M_2 n_2}{\rho}$$

$$\overline{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{n_1} = \frac{M_2}{\rho} - \frac{M_1 n_1 + M_2 n_2}{\rho^2}\cdot\left(\frac{\partial \rho}{\partial n_2}\right)_{n_1}$$

(b) $$x_2 = \frac{n_2}{n_1 + n_2} \Rightarrow \left(\frac{\partial x_2}{\partial n_2}\right)_{n_1} = \frac{n_1}{(n_1 + n_2)^2}$$

$$\left(\frac{\partial \rho}{\partial n_2}\right)_{n_1} = \frac{d\rho}{dx_2}\cdot\left(\frac{\partial x_2}{\partial n_2}\right)_{n_1} = \frac{n_1}{(n_1 + n_2)^2}\cdot\frac{d\rho}{dx_2}$$

$$\overline{V}_2 = \frac{M_2}{\rho} - \frac{M_1 n_1 + M_2 n_2}{\rho^2}\cdot\frac{n_1}{(n_1 + n_2)^2}\cdot\frac{d\rho}{dx_2} = \frac{M_2}{\rho} - (M_1 x_1 + M_2 x_2)\cdot\frac{x_1}{\rho^2}\cdot\frac{d\rho}{dx_2}$$

(c) Differentiating the given equation for ρ:

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$$\frac{d\rho}{dx_2} = -0.28930 + 0.59814 \cdot x_2 - 1.82628 \cdot x_2^2 + 2.37752 \cdot x_2^3 - 1.02905 \cdot x_2^4$$

When $x_2 = 0.100$, $\rho = 0.97061\ g\ cm^{-3}$ and $\frac{d\rho}{dx_2} = -0.24547\ g\ cm^{-3}$

Substituting these values and $M_1 = 18.016\ g\ mole^{-1}$, $M_2 = 32.043\ g\ mole^{-1}$, $x_1 = 0.900$ into the result of (b), $\overline{V}_2 = 37.56\ cm^3\ mole^{-1}$

1.5.6. Suppose that the density of a solution, in ($g\ cm^{-3}$), is known as a function of the concentration, c, of solute expressed in ($mole\ l^{-1}$) that is, that $\rho = \rho(c)$ if $c = \frac{1000 \cdot n_2}{\mathbf{V}}$ and n_2 is the number of moles of solute and **V** is the volume of solution in cm^3.

(a) Show that the volume of solute will be given by the expression:

$$\overline{V}_2 = \frac{M_2 - 1000 \cdot \frac{\partial \rho}{\partial c}}{\rho - c \cdot \frac{\partial \rho}{\partial c}}$$

(b) Show that the partial molar volume of solvent will be given (in cm^3) by the expression:

$$\overline{V}_1 = \frac{M_1}{\rho - c \cdot \frac{\partial \rho}{\partial c}}$$

Solution

(a) $\mathbf{m} = n_1 \cdot M_1 + n_2 \cdot M_2$ $\qquad c = \frac{1000 \cdot n_2}{\mathbf{V}} = \frac{1000 \cdot m}{\mathbf{V}}$, where m is molality

$$\rho = \frac{\mathbf{m}}{\mathbf{V}} = \frac{n_1 \cdot M_1 + n_2 \cdot M_2}{\mathbf{V}} = \frac{1000 + m \cdot M_2}{\mathbf{V}} \Rightarrow \mathbf{V} = \frac{1000 + m \cdot M_2}{\rho}$$

$$\overline{V}_2 = \left(\frac{\partial \mathbf{V}}{\partial n_2}\right)_{n_1} = \left(\frac{\partial \mathbf{V}}{\partial m}\right)_{n_1}$$

$$\overline{V}_2 = \frac{M_2 \cdot \rho - (1000 + m \cdot M_2) \cdot \frac{\partial \rho}{\partial m}}{\rho^2} = \frac{M_2 \cdot \rho - \rho \cdot V \cdot \frac{\partial \rho}{\partial m}}{\rho^2} = \frac{M_2 - V \cdot \frac{\partial \rho}{\partial m}}{\rho}$$

But $\qquad \frac{\partial \rho}{\partial m} = \frac{\partial \rho}{\partial c} \cdot \frac{\partial c}{\partial m}$

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$$\frac{\partial c}{\partial m}=1000\cdot\left(\frac{V-m\cdot\frac{\partial V}{\partial m}}{V^2}\right)=1000\cdot\frac{V\cdot\left(1-\frac{m}{V}\cdot\overline{V}_2\right)}{V^2}=\frac{1000}{V}\cdot\left(1-\frac{c}{1000}\cdot\overline{V}_2\right)$$

$$\frac{\partial\rho}{\partial m}=\frac{1000}{V}\cdot\left(1-\frac{c}{1000}\cdot\overline{V}_2\right)\cdot\frac{\partial\rho}{\partial c}$$

$$\overline{V}_2=\frac{M_2-V\cdot\frac{\partial\rho}{\partial m}}{\rho}\Rightarrow\overline{V}_2\cdot\rho=M_2-V\cdot\frac{\partial\rho}{\partial m}\Rightarrow$$

$$\overline{V}_2\cdot\rho=M_2-V\cdot\frac{1000}{V}\cdot\left(1-\frac{c}{1000}\cdot\overline{V}_2\right)\cdot\frac{\partial\rho}{\partial c}\Rightarrow\overline{V}_2\cdot\rho=M_2-1000\cdot\frac{\partial\rho}{\partial c}+c\cdot\overline{V}_2\cdot\frac{\partial\rho}{\partial c}$$

$$\Rightarrow\ \overline{V}_2=\frac{M_2-1000\cdot\frac{\partial\rho}{\partial c}}{\rho-c\cdot\frac{\partial\rho}{\partial c}}$$

(b) $$\mathbf{V}=n_1\cdot\overline{V}_1+n_2\cdot\overline{V}_2\Rightarrow\overline{V}_1=\frac{\mathbf{V}-n_2\cdot\overline{V}_2}{n_1}\Rightarrow\overline{V}_1=\frac{\mathbf{V}-m\cdot\overline{V}_2}{n_1}$$

$$\overline{V}_1=\frac{\mathbf{V}}{n_1}\cdot\left(1-\frac{m}{\mathbf{V}}\cdot\overline{V}_2\right)=\frac{\mathbf{V}}{n_1}\cdot\left(1-\frac{c}{1000}\cdot\overline{V}_2\right)$$

$$\mathbf{V}=\frac{m}{\rho}=\frac{1000+m\cdot M_2}{\rho}=\frac{1000+\frac{c\cdot\mathbf{V}}{1000}\cdot M_2}{\rho}\Rightarrow\mathbf{V}=\frac{1000}{\rho-\frac{c\cdot M_2}{1000}}$$

$$\overline{V}_1=\frac{\mathbf{V}}{n_1}\cdot\left(1-\frac{c}{1000}\cdot\overline{V}_2\right)=\frac{1}{n_1}\cdot\frac{1000}{\rho-\frac{c\cdot M_2}{1000}}\cdot\left(1-\frac{c}{1000}\cdot\frac{M_2-1000\cdot\frac{\partial\rho}{\partial c}}{\rho-c\cdot\frac{\partial\rho}{\partial c}}\right)$$

$$\Rightarrow\qquad\overline{V}_1=\frac{M_1}{\rho-c\cdot\frac{\partial\rho}{\partial c}}$$

1.5.7. The density of aqueous ammonium nitrate solutions at 25^0C is given by the following function of the molar concentration

$$\rho=0.99708+3.263\times10^{-2}\cdot c-9.63\times10^{-4}\cdot c^{3/2}-4.73\times10^{-6}\cdot c^2\ \ g\,cm^{-3}$$

Calculate $\overline{V}_1$ and $\overline{V}_2$ for c = 0; 0.1; 0.5 and 1.0 molar.

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Solution

Using the results obtained in problem 1.5.6:

$$\bar{V}_1 = \frac{M_1}{\rho - c \cdot \frac{\partial \rho}{\partial c}} \qquad \text{and} \qquad \bar{V}_2 = \frac{M_2 - 1000 \cdot \frac{\partial \rho}{\partial c}}{\rho - c \cdot \frac{\partial \rho}{\partial c}}$$

$$\frac{\partial \rho}{\partial c} = 0.03263 - 0.0014445 \cdot c^{1/2} - 0.0000946 \cdot c$$

The obtained values are presented in the following table:

c (*mole* l^{-1})	ρ ($g\ cm^{-3}$)	$\partial\rho/\partial c$	$\bar{V}_1$ ($cm^3\ mole^{-1}$)	$\bar{V}_2$ ($cm^3\ mole^{-1}$)
0	0.99708	0.03263	18.06775	47.508
0.1	1.00031	0.03216	18.06747	47.975
0.5	1.01301	0.03156	18.06450	48.570
1.0	1.02869	0.03109	18.05810	49.027

1.5.8. The apparent specific volume ($g\ cm^{-3}$) of component 2 in a solution is defined as:

$\phi_2 = \frac{V - w_1 \cdot v_1^0}{w_2}$ where V is the volume of the solution, v_1^0 is the specific volume of pure component 1, and w_1, w_2 are the weights (in grams) of the two components. We shall take w_1 to be 1 g, so that w_2 is the weight ratio of component 2 to component 1.

(a) Obtain an equation for $\partial\phi_2/\partial w_2$ in terms of the densities ρ of the solution and ρ_1^0 of pure component 1, w_2 and $\partial\rho/\partial w_2$.

(b) Use equation to evaluate the partial specific volume $\bar{v}_2$ of glycerol in a 50 percent (by weight) aqueous solution given the following densities:

Weight percent glycerol	0	49	50
Density of solution ($g\ cm^{-3}$)	0.9982	1.1236	1.1263

Solution

(a) $V = \frac{1 + w_2}{\rho}, \quad v_1^0 = \frac{1}{\rho_1^0}$

$$\phi_2 = \frac{V - v_1^0}{w_2} = \frac{1}{\rho} \cdot \left(\frac{1}{w_2} + 1 \right) - \frac{1}{\rho_1^0 \cdot w_2} = \frac{1}{w_2} \cdot \left(\frac{1}{\rho} - \frac{1}{\rho_1^0} \right) + \frac{1}{\rho}$$

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$$\frac{\partial \phi_2}{\partial w_2} = \left(\frac{1}{\rho} - \frac{1}{\rho_1^0} \right) - \frac{1}{w_2^2} - \frac{1}{\rho^2} \cdot \frac{\partial \rho}{\partial w_2} \cdot \left(\frac{1}{w_2} + 1 \right)$$

(b) $V = w_2 \cdot \phi_2 + v_1^0$

$$\bar{v}_2 = \frac{\partial V}{\partial w_2} = \phi_2 + w_2 \cdot \frac{\partial \phi_2}{\partial w_2}$$

Here $\rho = 1.1263\ g\ cm^{-3}$, $\rho_1^0 = 0.9982\ g\ cm^{-3}$, $w_2 = 1$

$$\frac{\partial \rho}{\partial w_2} \approx \frac{\Delta \rho}{\partial w_2} = \frac{1.1263 - 1.1236}{1 - \left(49/51 \right)} = 0.069\ g\ cm^{-3}$$

Then

$$\phi_2 = 0.774\ cm^3\ g^{-1},\ \frac{\partial \phi_2}{\partial w_2} = 0.0099\ cm^3\ g^{-1},\ \bar{v}_2 = 0.774 + 0.0099 = 0.784\ cm^3\ g^{-1}$$

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1.6. LAWS OF THERMOCHEMISTRY

1.6.1. HEATS OF CHEMICAL AND PHYSICAL PROCESSES. HEATS OF DISSOLUTION, DILUTION AND MIXTURE

1.6.1.1. One-tenth (0.1000) of a mole of liquid benzene, C_6H_6 (l), is burned in a bomb calorimeter at an initial temperature of 20^0C. If the heat of combustion (ΔH) of liquid benzene at 20^0C is – 782.3 *kcal mole*$^{-1}$ and if the heat capacity of the calorimeter and its contents is 5,000 *cal deg*$^{-1}$, what rise in temperature will be observed in the calorimeter if radiation losses are negligible?

Solution

$$\Delta H = \frac{Q}{n} = \frac{C \cdot \Delta T}{n} \Rightarrow \Delta T = \frac{n \cdot \Delta H}{C} = \frac{0.1 \times 782.3}{5} = 15.646 \,\text{deg}$$

1.6.1.2. In a determination of the enthaply of combustion of naphthalene ($C_{10}H_8$) by oxygen bomb calorimetry was found that the temperature of the calorimeter system rose 4.0630^0C on the combustion of a 1.1226 *g* sample of naphthalene. The mean temperature of the run was 18^0C. The temperature rise given here is corrected for the enthalpy of combustion of the cotton fuse and the formation of soot, carbon monoxide, and nitric acid. The heat capacity of the calorimeter system is 2660.0 *cal* and the formula weight of naphthalene is 128.11 *g mole*$^{-1}$. Calculate the enthalpy of combustion per mole of naphthalene at 18^0C.

Solution

$$C_{10}H_8(s) + 12 \cdot O_2(g) \rightarrow 10 \cdot CO_2(g) + 4 \cdot H_2O(l)$$

$$\Delta E = \frac{-2660.0 \times 4.0630 \times 128.11}{1.1226} = -1231.6 \, kcal \, mole^{-1}$$

$$\Delta H = \Delta E + (\Delta n_{gas})RT \qquad \Delta n_{gas} = -2$$

$$\Delta H = -1231.6 - 2 \times 1.987 \times 291.15 \times 10^{-3} = -1232.75 \, kcal \, mole^{-1}$$

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1.6.1.3. The heat of combustion (ΔH) of tungsten carbide at 300 K is – 285.65 *kcal mole*$^{-1}$ and the reaction is:

$$WC(s)+\frac{5}{2}O_2(g)=WO_3(s)+CO_2(g)$$

Compute the heat of the same reaction if it takes place in a constant volume bomb calorimeter at 300 *K*. Assume that the gases behave ideally and that corrections to standard states are negligible for solid species.

Solution

$$\Delta H=\Delta E+P\Delta V=\Delta E+(\Delta n_{gas})RT\Rightarrow\Delta E=\Delta H-(\Delta n_{gas})RT;\qquad \Delta n_{gas}=1-\frac{5}{2}=-\frac{3}{2}=-1.5$$

$$\Delta E=-285.65+1.5\times1.987\times10^{-3}\times300=-284.75\ \ kcal\cdot mole^{-1}$$

1.6.1.4. The heat involved in the solution of one mole of iron in dilute hydrochloric acid at constant pressure is - 20,800 *cal* at 18^0C. What is the change in internal energy of the system?

Solution

$$Fe(s)+2\cdot HCl(l)=FeCl_2(s)+H_2(g)$$

$$\Delta H=\Delta E+P\Delta V=\Delta E+(\Delta n_{gas})RT\Rightarrow\Delta E=\Delta H-(\Delta n_{gas})RT;\qquad \Delta n_{gas}=1$$

$$\Delta E=-20{,}800-1\times1.987\times291=-21{,}378\ \ cal$$

1.6.1.5. The heat of combustion of heptane (C_7H_{16}) at 27^0C determined in a constant volume bomb calorimeter is – 1,100 *kcal mole*$^{-1}$. What is the heat of combustion at constant pressure?

Solution

$$C_7H_{16}(l)+11\cdot O_2(g)=7\cdot CO_2(g)+8\cdot H_2O(l)$$

$$\Delta H=\Delta E+(\Delta n_{gas})RT=-1{,}100-4\times1.987\times10^{-3}\times300=-1{,}1024\ \ kcal\cdot mole^{-1}$$

1.6.1.6. The calorific value of food (actually the enthalpy of combustion of the food per unit mass) may be determined by measuring the heat produced by burning a weighed sample of food under constant-volume conditions in a bomb calorimeter. The heat released by the total combustion of a 1.00 *g* (3.00×10^{-3} *mole*) sample of chicken fat

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under these conditions (constant volume) was found to be 10,000 *cal* at 37^0C. Calculate the calorific value of the chicken fat in $cal.g^{-1}$ at 37^0C under constant pressure; that is, calculate the standard enthaply of combustion of the chicken fat at 37^0C. The reaction may be represented by the equation:

$$C_{20}H_{32}O_2(s) + 27 \cdot O_2(g) = 20 \cdot CO_2(g) + 16 \cdot H_2O(l)$$

Solution

$$\Delta H^0 = \Delta E^0 + (\Delta n_{gas})RT = 10{,}000 + (20 - 27) \times 3.00 \times 10^{-3} \times 1.987 \times 310.15 =$$
$$= 10{,}000 - 12.9 = 9{,}987 \ cal$$

1.6.1.7. A student made the following erroneous statement in a laboratory report on bomb calorimetry: "$\Delta H = \Delta E + P\Delta V$. Since the bomb calorimetry is a constant volume one, $\Delta V = 0$, and $\Delta H = \Delta E$". Explain why this argument is incorrect.

Solution

The error consists of applying an equation that is valid at constant pressure to a process that is being carried out at constant volume. In general:

$$H = E + PV \Rightarrow \Delta H = \Delta E + \Delta(PV)$$

At constant pressure, since $\Delta P = 0$ it follows that $\Delta H = \Delta E + P\Delta V$ and at constant volume (such as in bomb calorimetry), $\Delta V = 0$, and $\Delta H = \Delta E + V\Delta P$

1.6.1.8. (a) In an experiment to determine the enthaply of neutralization of HCl with NaOH, we mixed HCl and NaOH solutions in a precision calorimeter and the temperature of the contents of the calorimeter rose 0.2064^0C. The amount of water produced by the reaction was 3.4075 millimoles. Furthermore it was determined electrically that the capacity of the calorimeter and its contents was 223.9 $cal.^0C^{-1}$. Calculate the enthaply of neutralization per mole HCl. It is necessary to add algebraically a correction of +155 cal mole H_2O produced to the final result to adjust for the enthalpy of mixing HCl and NaOH solutions before the reaction takes place.

(b) In another experiment was found that the enthaply of neutralization of $HClO_4$ is, within experimental error, the same as that of HCl. On the other hand the enthaply of neutralization of acetic acid with NaOH is –13.300 $kcal\ mole^{-1}$. How do you account

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for the fact that the enthaplies of neutralization of HCl and $HClO_4$ are identical but different from of acetic acid?

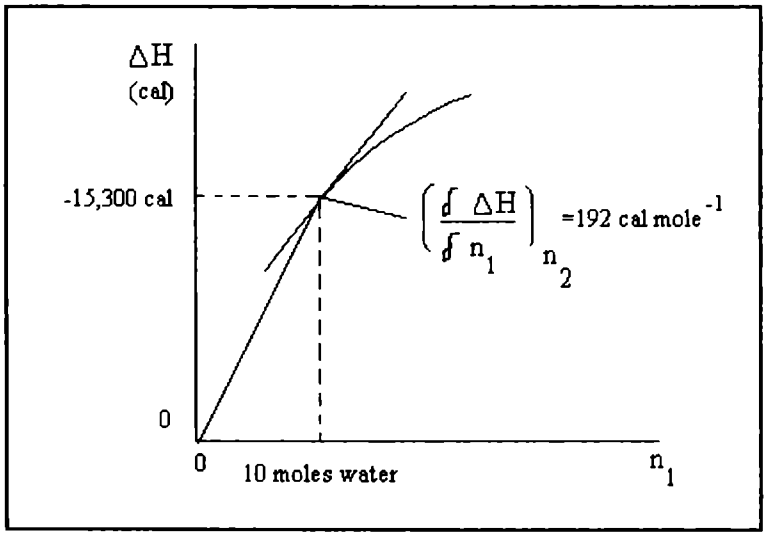
Solution

(a) $$\Delta H = \frac{C_P \Delta T}{moles\ H_2O\ formed} + correction = \frac{-223.9 \times 10^{-3} \times 0.2064}{3.4075 \times 10^{-3}} + 0.155$$

$$\Delta H = -13.562 + 0.155 = -13.4\ kcal \cdot mole^{-1}$$

(b) HCl and $HClO_4$ are strong acids and complete dissociated. Acetic acid is a weak acid and is partially dissociated. The difference between the observed enthaply is equal to the enthaply of dissociation of acetic acid.

1.6.1.9. The graph gives the integral heat of solution in water at 18^0C. Determine the differential heat of solute, $\overline{\Delta H_2}$, for a solution containing 1 mole of H_2SO_4 in 10 moles of H_2O.



Solution

See figure in problem

$$\Delta H = n_1 \cdot \overline{\Delta H_1} + n_2 \cdot \overline{\Delta H_2} = -192 \times 10 + 1 \cdot \overline{\Delta H_2} = -15{,}300 \Rightarrow \overline{\Delta H_2} = -13{,}380\ cal$$

1.6.1.10. At 25^0C the integral heat of solution of a certain acid in water is given by the formula:

$$\Delta H(cal) = 2.00 \cdot n_1^{1/2} + 3.00 \cdot n_1^{3/2} + 4.00 \cdot n_1^{5/2}$$

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where n_1 is the number of moles of water per mole of acid. Evaluate $\overline{\Delta H}_2$ (that is $\left(\partial \Delta H / \partial n_2\right)_{P,T,n_1}$) for a solution that is 9 mole percent acid.

Solution

$n_1 = 9$; $n_2 = 1$

$$\Delta H = 2.00 \cdot (9)^{1/2} + 3.00 \cdot 9^{3/2} + 4.00 \cdot (9)^{5/2} = 1059 \ cal$$

$$\overline{\Delta H_1} = \left(\frac{\partial H}{\partial n_1}\right)_{P,T,n_2} = \frac{1}{2} \times 2.00 \cdot n_1^{-1/2} + \frac{3}{2} \times 3.00 \cdot n_1^{1/2} + \frac{5}{2} \times 4.00 \cdot n_1^{3/2} =$$

$$= 1.00 \cdot (9)^{-1/2} + 4.50 \cdot 9^{1/2} + 10.00 \cdot (9)^{3/2} = 284 \ cal \cdot mole^{-1}$$

$$n_2 \cdot \overline{\Delta H_2} = \Delta H - n_1 \cdot \overline{\Delta H_1} \Rightarrow 1 \cdot \overline{\Delta H_2} = 1059 - 9 \times 284 = -1497 \Rightarrow$$

$$\overline{\Delta H_2} = -1497 \ cal \cdot mole^{-1}$$

1.6.1.11. The following data on the integral heats of solution of NaCl in water at $2^0 C$ were presented in the table:

m (moles NaCl per kg H_2O)	ΔH ($cal.mole^{-1}$)
0.0624	1846
0.2001	1780
0.4003	1650
0.7504	1531
1.0058	1439
1.9457	1187
3.1064	946
4.0012	767
4.9966	619
6.0004	454

How much heat would be absorbed upon adding 116 *g* of H_2O to 100 *g* of a solution, initially 10.0 weight percent NaCl, at this temperature?

Solution

Moles H_2O/mole NaCl = 889, 280, 139, 73.9, 55.2, 28.5, 17.9, 13.9, 11.1, 9.25.

Plot ΔH versus moles H_2O/mole NaCl (see figure). Draw a smooth curve through data points.

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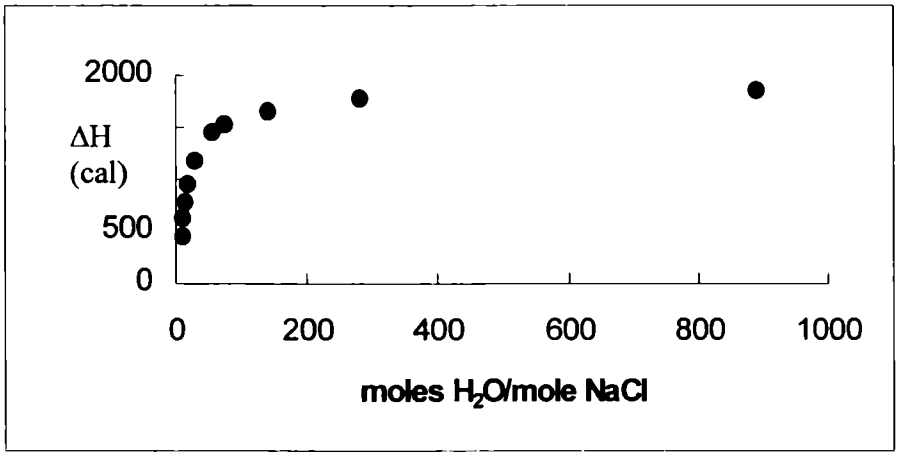

The initial concentration of the solution = (90/18.0)/(10/58.5) = 29.2 moles H_2O/mole NaCl. At this concentration ΔH = 1195 $cal.mole^{-1}$ (from graph). The final concentration of the solution = (216/18.0)/(10/58.5) = 70.3 moles H_2O/mole NaCl. At this concentration ΔH = 1518 $cal.mole^{-1}$ (from graph).

$$d(\Delta H) = \frac{10}{58.5} \cdot (1518 - 1195) = 55.2 \ cal$$

1.6.1.12. Using data from the table below (compound 1 = H_2O, compound 2 = H_2SO_4) calculate the following:

(a) The total amount of heat released when 4 moles of H_2O are added to a solution consisting initially of 6 moles of H_2O and 1 mole of H_2SO_4

(b) The total amount of heat released when 3 moles of H_2O are mixed with 6 moles of H_2SO_4.

Integral and Differential Heats of Solution for 1 Mole of H_2SO_4 in Water at 25^0C

Moles H_2O (n_1)	ΔH (cal)	$\overline{\Delta H_1}$ ($cal \cdot mole^{-1}$)	$\overline{\Delta H_2}$ ($cal \cdot mole^{-1}$)
0	0	-6,750	0
0.5	-3,810	-6.740	-438
1	-6,820	-4,730	-2,090
2	-9,960	-2,320	-5,320
3	-11,890	-1,480	-7,450
4	-13,120	-1,040	-8,960
6	-14,740	-570	-11,320
10	-16,240	-233	-13,910

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Solution

(a) The initial composition of the solution = 6 moles H_2O per mole of H_2SO_4 and the final composition = 10 moles H_2O per mole of H_2SO_4.

$$\Delta H = -16{,}240 - (-14{,}740) = -1500 \ cal$$

(b) (3 moles H_2O)/(6 moles H_2SO_4) = 0.5 moles H_2O per mole of H_2SO_4

$$\overline{\Delta H_1} = -6740 \ cal \cdot mole^{-1} \quad \text{and} \quad \overline{\Delta H_2} = -438 \ cal \cdot mole^{-1}$$

$$\Delta H = n_1 \cdot \overline{\Delta H_1} + n_2 \cdot \overline{\Delta H_2} = (-6{,}740 \times 3) + (-438 \times 6) = -22{,}848 \ cal$$

1.6.1.13. (a) Calculate the heat of mixing of 2 (HCl·50 Aq) with 1 (HCl·200 Aq) at 25^0C;

(b) If 3 HCl (g) is now dissolved in the resulting solution, what is the additional heat effect? Use the following enthalpy data, which are valid at 25^0C.

HCl (g)	-22.06 *kcal*
HCl·50 Aq	-39.52 *kcal*
HCl·100 Aq	-39.66 *kcal*
HCl·200 Aq	-39.74 *kcal*

Solution

(a) $2 \cdot HCl \cdot 50 \cdot Aq + 1 \cdot HCl \cdot 200 \cdot Aq = 3 \cdot HCl \cdot 100 \cdot Aq \qquad \Delta H_x$

$HCl(g) + 50 \cdot Aq = HCl \cdot 50 \cdot Aq \qquad \Delta H_1 = -39.52 \ kcal$

$HCl(g) + 100 \cdot Aq = HCl \cdot 100 \cdot Aq \qquad \Delta H_2 = -39.66 \ kcal$

$HCl(g) + 200 \cdot Aq = HCl \cdot 200 \cdot Aq \qquad \Delta H_3 = -39.74 \ kcal$

$$\Delta H_x = -2 \times \Delta H_1 + 3 \times \Delta H_2 - \Delta H_3 = -2 \times (-39.52) + 3 \times (-39.66) - (-39.74) = -0.2 \ kcal$$

(b) $3 \cdot HCl \cdot 100 \cdot Aq + 3 \cdot HCl(g) = 6 \cdot HCl \cdot 50 \cdot Aq \qquad \Delta H_y$

$HCl(g) + 50 \cdot Aq = HCl \cdot 50 \cdot Aq \qquad \Delta H_1 = -39.52 \ kcal$

$HCl(g) + 100 \cdot Aq = HCl \cdot 100 \cdot Aq \qquad \Delta H_2 = -39.66 \ kcal$

$\frac{1}{2} \cdot H_2(g) + \frac{1}{2} \cdot Cl_2(g) = HCl(g) \qquad \Delta H_4 = -22.06 \ kcal$

$$\Delta H_y = 6 \times \Delta H_1 - 3 \times \Delta H_2 - 3 \times \Delta H_4 = 6 \times (-39.52) - 3 \times (-39.66) - 3 \times (-22.06) = -51.96 \ kcal$$

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1.6.2. HESS'S LAW

1.6.2.1. Given the following heats of formation at 25^0C:

$BaCl_2 \cdot 100$ Aq	-207.803 *kcal*
$BaCl_2 \cdot 300$ Aq	-207.905 *kcal*
$BaCl_2 \cdot 500$ Aq	-207.963 *kcal*

If 1 $BaCl_2 \cdot 100$ Aq is dissolved in 1 $BaCl_2 \cdot 500$ Aq, what is ΔH for the process?

Solution

$$BaCl_2 \cdot 100 \cdot Aq + BaCl_2 \cdot 500 \cdot Aq = 2 \cdot BaCl_2 \cdot 300 \cdot Aq$$

$$\Delta H = 2 \cdot \Delta H_{BaCl_2 \cdot 300 \cdot Aq} - \Delta H_{BaCl_2 \cdot 100 \cdot Aq} - \Delta H_{BaCl_2 \cdot 500 \cdot Aq} = -0.044 \ kcal$$

1.6.2.2. The enthalpies of formation of the following compounds at 15^0C are: PbO, -50.30 *kcal*; SO_2, -70.92 *kcal*; PbS, 19.30 *kcal*. Calculate ΔH and ΔE for the reaction $PbS(s) + 2 \cdot PbO(s) \rightarrow 3 \cdot Pb(s) + SO_2(g)$ at the same temperature.

Solution

$$\Delta H = 3 \cdot \Delta H_{Pb} + \Delta H_{SO_2} - \Delta H_{PbS} - 2 \cdot \Delta H_{PbO} = -70.92 - 19.30 + 2 \times 50.3 = 10.38 \ kcal$$

$$\Delta H = \Delta E + P\Delta V = \Delta E + \Delta nRT \Rightarrow$$

$$\Delta E = \Delta H - \Delta nRT = 10.38 - 1 \times 1.987 \times 10^{-3} \times 288 = 9.81 \ kcal$$

1.6.2.3. Calculate the heat of formation of solid aluminum chloride (Al_2Cl_6) from the following data:

$Al(s) + 3 \cdot HCl(aq) \rightarrow AlCl_3(aq) + \frac{3}{2} \cdot H_2(g)$	$\Delta H_1 = -127.0 \ kcal$
$H_2(g) + Cl_2(g) \rightarrow 2 \cdot HCl(g)$	$\Delta H_2 = -44.0 \ kcal$
$HCl(g) + aq \rightarrow HCl(aq)$	$\Delta H_3 = -17.5 \ kcal$
$Al_2Cl_6(s) + aq \rightarrow 2 \cdot AlCl_3(aq)$	$\Delta H_4 = -155.8 \ kcal$

Solution

$$2 \cdot Al(s) + 3 \cdot Cl_2(g) \rightarrow Al_2Cl_6(s) \qquad \Delta H_x$$

$$\Delta H_x = 2 \cdot \Delta H_1 + 3 \cdot \Delta H_2 + 6 \cdot \Delta H_3 - \Delta H_4 = -335.2 \ kcal$$

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1.6.2.4. The enthalpies of solution in 1.000 N HCl of certain compounds of the type $n\text{CaO}\cdot m\text{B}_2\text{O}_3$ at 298K are as follows:

Compound	Enthaply of Solution in 1.000 N HCl ($cal\cdot mole^{-1}$)
$3\text{CaO}\cdot\text{B}_2\text{O}_3$	$\Delta H_1 = -82{,}423$
$2\text{CaO}\cdot\text{B}_2\text{O}_3$	$\Delta H_2 = -50{,}287$
$\text{CaO}\cdot\text{B}_2\text{O}_3$	$\Delta H_3 = -20{,}259$
$\text{CaO}\cdot 2\text{B}_2\text{O}_3$	$\Delta H_4 = -10{,}080$
CaO	$\Delta H_5 = -46{,}380$
B_2O_3	$\Delta H_6 = -3286$

Calculate ΔH for the reaction $3\cdot CaO + B_2O_3 = 3\cdot CaO\cdot B_2O_3$

Solution

$$\Delta H_{298} = 3\cdot\Delta H_5 + \Delta H_6 - \Delta H_1 = -60{,}003\ cal$$

1.6.2.5. On the basis of the following enthalpy changes evaluate ΔH^0 for the ionization of aqueous m-chlorophenol (m-CP)

$$m-CP(l)\rightarrow m-CP(aq) \qquad \Delta H_1^0 = 674\ cal\cdot mole^{-1}$$

$$m-CP(l)+HO^-(aq)\rightarrow m-CP^-(aq)+H_2O(l) \qquad \Delta H_2^0 = -7450\ cal\cdot mole^{-1}$$

$$H_2O(l)\rightarrow H^+(aq)+HO^-(aq) \qquad \Delta H_3^0 = 13{,}500\ cal\cdot mole^{-1}$$

Solution

$$m-CP(aq)\rightarrow m-CP^-(aq)+H^+(aq)$$

$$\Delta H^0 = \Delta H_2^0 - \Delta H_1^0 + \Delta H_3^0 = -7450 - 674 + 13{,}500 = 5286\ cal/mole\ m-CP(aq)$$

1.6.2.6. Calculate the heat of formation of a mole of gaseous water using the heats of the following reactions:

$$H_2(g)+\frac{1}{2}\cdot O_2(g)=H_2O(g) \qquad \Delta H_I^0 = -57{,}800\ cal$$

$$H_2(g)=2\cdot H(g) \qquad \Delta H_{II}^0 = 103{,}800\ cal$$

$$O_2(g)=2\cdot O(g) \qquad \Delta H_{III}^0 = 117{,}400\ cal$$

Solution

$$2\cdot H(g)+O(g)=H_2O(g) \qquad \Delta H_{IV}^0 = ?\ cal$$

$$\Delta H_{IV}^0 = -57{,}800 - 103{,}800 - 58{,}700 = -220{,}300\ cal$$

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1.6.3. HEAT OF COMBUSTION – HEAT OF FORMATION CORRELATION

1.6.3.1. At 25^0C the molar heat of combustion of benzoic acid is – 771.4 *kcal*. The heats of formation of CO_2 (g) and H_2O (l) at 25^0C are – 94.05 and – 68.32 *kcal* respectively.

(a) Calculate the heat of formation of 1 mole of benzoic acid;

(b) How much heat is liberated if 1 mole of benzoic acid is burned in a bomb calorimeter at 25^0C?

Solution

(a) $C_6H_5COOH(s)+\frac{15}{2}\cdot O_2(g)=7\cdot CO_2(g)+3\cdot H_2O(l) \qquad \Delta H=-771.4\ kcal$

$$\Delta H=7\cdot\Delta H_{f,CO_2(g)}+3\cdot\Delta H_{f,H_2O(l)}-\Delta H_{f,C_6H_5COOH(s)}-\frac{15}{2}\cdot\Delta H_{f,O_2(g)}\Rightarrow$$

$$\Delta H_{f,C_6H_5COOH(s)}=7\cdot\Delta H_{f,CO_2(g)}+3\cdot\Delta H_{f,H_2O(l)}+\frac{15}{2}\cdot\Delta H_{f,O_2(g)}-\Delta H\Rightarrow$$

$$\Delta H_{f,C_6H_5COOH(s)}=7\cdot(-94.05)+3\cdot(-68.32)+0+771.4=-91.91\ kcal$$

(b) $Q=\Delta E+P\Delta V$

In a bomb calorimeter, the reaction is taking place at constant volume. Therefore, when V = constant, $\Delta V=0\Rightarrow Q_V=\Delta E$

$$\Delta H=\Delta E+P\Delta V=\Delta E+\Delta nRT\Rightarrow\Delta E=\Delta H-\Delta nRT$$

$$\Delta n=7-\frac{15}{2}=-0.5$$

$$\Delta E=-771.4+0.5\times1.987\times10^{-3}\times298.15=-771.104\ kcal$$

1.6.3.2. At 298.16 K the standard enthalpy of combustion of cis-hexahydroindan (C_9H_{16}) is –1351.60 *kcal·mole*$^{-1}$. The combustion process may be represented by the equation:

$$cis-C_9H_{16}(l)+13\cdot O_2(g)\rightarrow 9\cdot CO_2(g)+8\cdot H_2O(l)$$

(a) Calculate the standard enthalpy of formation of 1 mole of cis-hexahydroindan from the elements at 298.16 K.

(b) How would the answer be changed if diamond instead of graphite were chosen as the standard state of C?

$$C(diamond)\rightarrow C(graphite) \qquad \Delta H^0_{298}=-0.45\ kcal$$

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Solution

(a) $cis-C_9H_{16}(l)+13\cdot O_2(g)\rightarrow 9\cdot CO_2(g)+8\cdot H_2O(l)$ $\quad \Delta H_1^0=-1351.60\ kcal$

$C(graphite)+O_2(g)\rightarrow CO_2(g)$ $\quad \Delta H_2^0=-94.0518\ kcal$

$H_2(g)+\frac{1}{2}\cdot O_2(g)\rightarrow H_2O(l)$ $\quad \Delta H_3^0=-68.3174\ kcal$

$9\cdot C(graphite)+8\cdot H_2(g)\rightarrow cis-C_9H_{16}(l)$ $\quad \Delta H_4^0=?$

By applying Hess's law:

$\Delta H_4^0=-\Delta H_1^0+9\cdot\Delta H_2^0+8\cdot\Delta H_3^0=1351.6+9\times(-94.0518)+8\times(-68.3174)\Rightarrow$

$\Delta H_4^0=1351.60-846.4662-546.5392=-41.41\ kcal\cdot mole^{-1}$

(b) Usually graphite is taken to be the standard state of carbon but if diamond were chosen instead, the new standard enthalpy of formation of CO_2 (g) would be:

$C(graphite)+O_2(g)\rightarrow CO_2(g)$ $\quad \Delta H_2^0=-94.0518\ kcal$

$C(diamond)\rightarrow C(graphite)$ $\quad \Delta H_{298}^0=-0.45\ kcal$

$C(diamond)+O_2(g)\rightarrow CO_2(g)$ $\quad \Delta H_2^{0'}=-94.5018\ kcal$

and ΔH_4^0 for the formation of cis-hexahydroindan would be – 45.46 $kcal\cdot mole^{-1}$.

1.6.3.3. The standard enthalpy of combustion of aluminium hydride, $Al(BH_4)_3$ (l), was found to be – 989.1 $kcal\cdot mole^{-1}$ at 298.2 K, the reaction being:

$$Al(BH_4)_3(l)+6\cdot O_2(g)\rightarrow\frac{1}{2}\cdot Al_2O_3(crystal,corundun)+\frac{3}{2}\cdot B_2O_3(crystal)+6\cdot H_2O(l)$$

Calculate the standard enthalpy of formation of $Al(BH_4)_3$ (g). The enthalpy of vaporization of $Al(BH_4)_3$ (l) is 7.2 $kcal\cdot mole^{-1}$ and the standard enthalpies of formation of some other compound necessary for the calculation are as follow:

$\Delta H_{Al_2O_3(crystal.corundun)}=-399.09\ kcal\cdot mole^{-1}$ and $\Delta H_{B_2O_3(crystal)}=-303\ kcal\cdot mole^{-1}$

Solution

$$\Delta H_f^0=\frac{1}{2}\times(-399.09)+\frac{3}{2}\times(-303)+6\times(-68.3174)-(-989.1)+7.2=-67.7\ kcal\cdot mole^{-1}$$

Experimentally, the value – 72.1 $kcal\cdot mole^{-1}$ was found.

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1.6.3.4. Given the following data:

$$C(s)+O_2(g)\rightarrow CO_2(g) \qquad \Delta H_1^0=-94.05\ kcal$$

$$H_2(g)+\frac{1}{2}\cdot O_2(g)\rightarrow H_2O(l) \qquad \Delta H_2^0=-68.32\ kcal$$

$$CH_2N_2(s)+\frac{3}{2}\cdot O_2(g)\rightarrow CO_2(g)+H_2O(l)+N_2(g) \qquad \Delta H_3^0=-177.20\ kcal$$

Compute the standard enthalpy of formation of cyanamide, CH_2N_2 (s).

Solution

$$C(s)+H_2(g)+N_2(g)\rightarrow CH_2N_2(s) \qquad \Delta H_x=?$$

$$\Delta H_x=\Delta H_1^0+\Delta H_2^0-\Delta H_3^0=-94.05-68.32+177.20=14.83\ kcal\cdot mole^{-1}$$

1.6.3.5. The standard enthalpy of combustion of solid naphthalene ($C_{10}H_8$) is $\Delta H_{298}^0=-1231.6\ kcal\cdot mole^{-1}$. The products are CO_2 and liquid H_2O. Find the standard enthalpy of formation of naphthalene.

Solution

The equation of the naphthalene combustion reaction is:

$$C_{10}H_8(s)+12\cdot O_2(g)\rightarrow 10\cdot CO_2(g)+4\cdot H_2O(l) \qquad \Delta H_1^0=-1231.6\ kcal\cdot mole^{-1}$$

$$C(s)+O_2(g)\rightarrow CO_2(g) \qquad \Delta H_2^0=-94.0518\ kcal\cdot mole^{-1}$$

$$H_2(g)+\frac{1}{2}\cdot O_2(g)\rightarrow H_2O(l) \qquad \Delta H_3^0=-68.3174\ kcal\cdot mole^{-1}$$

$$10\cdot C(s)+4\cdot H_2(g)\rightarrow C_{10}H_8(s) \qquad \Delta H_x=?$$

$$\Delta H_x=10\times\Delta H_2^0+4\times\Delta H_3^0-\Delta H_1^0=10\times(-94.0518)+4\times(-68.3174)+1231.6\Rightarrow$$

$$\Delta H_x=17.81\ kcal\cdot mole^{-1}$$

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1.6.4. HEAT OF REACTION, OR FORMATION – ENERGY OF CHEMICAL BOND CORRELATION

1.6.4.1. Let us find out the energies of C – H and C – C bonds using the heats of the following reactions:

$C(graphite) + 2 \cdot H_2(g) = CH_4(g)$ $\qquad \Delta H_I^0 = -15.99\ kcal$

$2 \cdot C(graphite) + 3 \cdot H_2(g) = C_2H_6(g)$ $\qquad \Delta H_{II}^0 = -16.52\ kcal$

$C(graphite) = C(g)$ $\qquad \Delta H_{III}^0 = 172.7\ kcal$

$H_2(g) = 2 \cdot H(g)$ $\qquad \Delta H_{IV}^0 = 103.05\ kcal$

Solution

Combining equations I – IV, we get:

$CH_4(g) = C(g) + 4 \cdot H(g)$ $\qquad \Delta H_V^0 = 394.80\ kcal$

$C_2H_6(g) = 2 \cdot C(g) + 6 \cdot H(g)$ $\qquad \Delta H_{VI}^0 = 671.10\ kcal$

The heats (energies) of dissociation into atoms at 0 K are equal to the sums of the energies of all bonds in a molecule.

$\Delta H_V^0 = 394.80\ kcal = 4 \cdot \varepsilon_{C-H} \Rightarrow \varepsilon_{C-H} = 98.7\ kcal \cdot mole^{-1}$

$\Delta H_{VI}^0 = 671.10\ kcal = \varepsilon_{C-C} + 6 \cdot \varepsilon_{C-H} \Rightarrow \varepsilon_{C-C} = 671.10 - 6 \times 98.7 = 78.9\ kcal \cdot mole^{-1}$

1.6.4.2. Heats of formation may be calculated from so-called bond energies. The approximate average bond energies at 25^0C are 104 $kcal \cdot mole^{-1}$ for H – H, 80 $kcal \cdot mole^{-1}$ for C – C and 99 $kcal \cdot mole^{-1}$ for C – H (see Table 2. of Appendicces). Calculate the standard heat of formation of propane at 25^0C. The heat of vaporization of carbon at 25^0C is 171 $kcal \cdot mole^{-1}$

Solution

The equation describing the formation of propane is:

$3 \cdot C(s) + 4 \cdot H_2(g) = C_3H_8(g)$ $\qquad \Delta H_x = ?$

From the problem data one can calculate the enthalpy for the reaction:

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$$3 \cdot C(g) + 4 \cdot H_2(g) = C_3H_8(g) \qquad \Delta H_1$$

$$\Delta H_1 = 4 \times \varepsilon_{H-H} - 2 \times \varepsilon_{C-C} - 8 \times \varepsilon_{C-H} = -536 \ kcal \cdot mole^{-1}$$

From this equation and the vaporization of C we can calculate ΔH_x.

$$C(s) = C(g) \qquad \Delta H_2 = 171 \ kcal \cdot mole^{-1}$$

$$\Delta H_x = \Delta H_1 + 3 \times \Delta H_2 = -536 + 3 \times 171 = -23 \ kcal \cdot mole^{-1}$$

1.6.4.3. The heat of formation of S_8 (g) at 25^0C is 24.45 $kcal \cdot mole^{-1}$ and that of S (g) is 25^0C is 66.636 $kcal \cdot mole^{-1}$. Calculate an enthalpy value for S – S bond assuming S_8 to consist of a ring of eight sulfur atoms joined together by single bonds.

Solution

$$8 \cdot S(g) \Leftrightarrow S_8(g)$$

$$\Delta H = \Delta H_{S_8} - 8 \cdot \Delta H_S = -8 \times \varepsilon_{S-S} \Rightarrow \varepsilon_{S-S} = \frac{8 \cdot \Delta H_S - \Delta H_{S_8}}{8} = \Delta H_S - \frac{\Delta H_{S_8}}{8} \Rightarrow$$

$$\Delta H = 66.636 - \frac{24.48}{8} = 63.576 \ kcal \cdot mole^{-1}$$

1.6.4.4. Using the bond enthalpies from the following table evaluate ΔH for the isomerization of ethyl alcohol to dimethylether.

$$CH_3 - CH_2 - OH(g) \rightarrow CH_3 - O - CH_3(g)$$

Empirical bond enthalpies at 25^0C	
Bond	ΔH $[kcal \cdot mole^{-1}]$
H – H	104
O – O	33
O – H	111
C – H	99
C – O	84
C – C	83

Solution

$$\varepsilon_{bonds\ broken} = \varepsilon_{O-H} + \varepsilon_{C-C} = 111 + 83 = 194 \ kcal \cdot mole^{-1}$$

$$\varepsilon_{bonds\ formed} = \varepsilon_{C-O} + \varepsilon_{C-H} = 84 + 99 = 183 \ kcal \cdot mole^{-1}$$

$$\Delta H = \varepsilon_{bonds\ broken} - \varepsilon_{bonds\ formed} = 194 - 183 = 11 \ kcal \cdot mole^{-1}$$

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1.6.4.5. At 298.2 K the standard enthalpy of formation of $Mg(NO_3)_2$ is – 188,770 $cal \cdot mole^{-1}$ and the standard enthalpy of solution is – 21,530 $cal \cdot mole^{-1}$; the standard enthalpy of formation of the NO_3^- ion is – 49,320 $cal\ (g\ ion)^{-1}$. Calculate the standard enthalpy of formation of the Mg^{2+} ion at this temperature.

Solution

$$Mg(s) + N_2(g) + 3 \cdot O_2(g) \rightarrow Mg(NO_3)_2(s)$$

$$\Delta H_1^0 = -188{,}770\ cal \cdot mole^{-1}$$

$$Mg(NO_3)_2(s) + aq \rightarrow Mg^{2+}(aq) + 2 \cdot NO_3^-(aq)$$

$$\Delta H_2^0 = -21{,}530\ cal \cdot mole^{-1}$$

$$\frac{1}{2} \cdot N_2(g) + \frac{3}{2} \cdot O_2(g) + e^- \rightarrow NO_3^-(aq)$$

$$\Delta H_3^0 = -49{,}320\ cal \cdot (g\ ion)^{-1}$$

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2 \cdot e^- \qquad \Delta H_f^0 = ?$$

$$\Delta H_f^0 = \Delta H_1^0 + \Delta H_2^0 - 2 \times \Delta H_3^0 = -188{,}770 - 21{,}530 + 2 \times 49{,}320 = -111{,}660\ cal(g\ ion)^{-1}$$

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1.6.5. KIRCHHOFF'S LAW

1.6.5.1. The molar heat capacities of Na (g), Cl_2 (g) and NaCl (s) at room temperature are respectively 6.73, 8.10 and 11.98 $cal \cdot deg^{-1}$. The heat of formation of NaCl (s) at 25^0C is –98.279 *kcal*. Calculate the heat of formation of NaCl (s) at 35^0C.

Solution

$$Na(g)+\frac{1}{2}\cdot Cl_2(g)=NaCl(s)$$

$$\Delta H_{T_2}=\Delta H_{T_1}+\int_{T_1}^{T_2}\Delta C_P dT$$

$$\Delta H_{308}=\Delta H_{298}+\int_{298}^{308}\left(C_{P_{NaCl}}-C_{P_{Na}}-\frac{1}{2}\cdot C_{P_{Cl_2}}\right)dT=-98279+\int_{298}^{308}\left(11.98-6.73-\frac{8.1}{2}\right)dT$$

$$\Delta H_{308}=-98279+1.2\times(308-298)=-98267\ cal \Rightarrow \Delta H_{308}=-98.267\ \text{k}cal$$

1.6.5.2. Given that the molar thermal capacity of oxygen at constant pressure over the temperature range concerned may be represented by the equation:

$$C_P=6.100+3.25\times10^{-3}\cdot T-1.02\times10^{-6}\cdot T^2 \quad \left(cal\cdot \deg^{-1}\cdot mole^{-1}\right)$$

Determine the quantity of heat required to raise the temperature of one mole of oxygen from 27^0C to 127^0C at 1 atmosphere pressure.

Solution

$$\Delta H=\int_{300}^{400}C_P dT=\int_{300}^{400}\left(6.100+3.25\times10^{-3}\cdot T-1.02\times10^{-6}\cdot T^2\right)dT \Rightarrow$$

$$\Delta H=\left(6.100\cdot T+\frac{3.25\times10^{-3}}{2}\cdot T^2-\frac{1.02\times10^{-6}}{3}\cdot T^3\right)\Big/_{300}^{400}=771.17\ cal$$

1.6.5.3. The increase in enthalpy during the reaction: $CaCO_3(s)=CaO(s)+CO_2(g)$ is 42,900 $cal \cdot mole^{-1}$ at 15^0C. Given that over the temperature range concerned the molar thermal capacities are almost independent of temperature :

CaO $\quad C_P=12.27\ cal\cdot \deg^{-1}$

$CaCO_3$ $\quad C_P=26.37\ cal\cdot \deg^{-1}$

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CO_2 $\quad C_P = 7.30\ cal \cdot \deg^{-1}$, calculate the values of ΔH and ΔE at $600^0 C$.

Solution

$$\Delta H_{873} = \Delta H_{288} + \int_{288}^{873} \Delta C_P dT = \Delta H_{288} + \int_{288}^{873} \left(C_{P_{CaO}} + C_{P_{CO_2}} - C_{P_{CaCO_3}}\right) dT \Rightarrow$$

$$\Delta H_{873} = 42{,}900 + \int_{288}^{873} (7.30 + 12.27 - 26.37) dT = 42{,}900 - 6.8 \times (873 - 288) \Rightarrow$$

$$\Delta H_{873} = 38{,}922\ cal \cdot mole^{-1}$$

$$\Delta H_{873} = \Delta E_{873} + \Delta nRT \Rightarrow \Delta E_{873} = \Delta H_{873} - \Delta nRT$$

$$\Delta E_{873} = 38{,}922 - 1 \times 1.987 \times 873 = 37{,}187\ cal \cdot mole^{-1}$$

1.6.5.4. Find the equation $\Delta H^0 = \varphi(T)$ and compute ΔH^0_{1000} for the reaction:

$CH_4(g) = C(s) + 2 \cdot H_2(g)$ $\quad$ if $\Delta H^0_{298} = 17880\ cal \cdot mole^{-1}$ and:

$$C_{P_{C(s)}} = 2.673 + 2.617 \times 10^{-3} \cdot T - 1.169 \times 10^5 \cdot T^{-2} \quad \left(cal \cdot \deg^{-1} \cdot mole^{-1}\right)$$

$$C_{P_{H_2(g)}} = 6.62 + 0.81 \times 10^{-3} \cdot T \quad \left(cal \cdot \deg^{-1} \cdot mole^{-1}\right)$$

$$C_{P_{CH_4(g)}} = 5.34 + 11.5 \times 10^{-3} \cdot T \quad \left(cal \cdot \deg^{-1} \cdot mole^{-1}\right)$$

Solution

According to Kirchhoff's law:

$$\Delta H^0_T = \Delta H^0_0 + \int_0^T \Delta C_P dT$$

$$\Delta C_P = C_{P_{C(s)}} + 2 \cdot C_{P_{H_2(g)}} - C_{P_{CH_4(g)}} = 10.573 - 7.263 \times 10^{-3} \cdot T - 1.169 \times 10^5 \cdot T^{-2}$$

$$\Delta H^0_T = \Delta H^0_0 + \int_0^T \left(10.573 - 7.263 \times 10^{-3} \cdot T - 1.169 \times 10^5 \cdot T^{-2}\right) dT \Rightarrow$$

$$\Delta H^0_T = \Delta H^0_0 + 10.573 \cdot T - \frac{7.263 \times 10^{-3}}{2} \cdot T^2 + 1.169 \times 10^5 \cdot T^{-1}$$

Using the value of ΔH^0_{298}, we compute ΔH^0_0 according to the derived equation:

$$\Delta H^0_0 = \Delta H^0_{298} - 10.573 \cdot 298 + \frac{7.263 \times 10^{-3}}{2} \cdot 298^2 - 1.169 \times 10^5 \cdot 298^{-1} \Rightarrow$$

$$\Delta H^0_0 = 14659.45\ cal \cdot mole^{-1}$$

We finally get the expression for ΔH^0_T:

$$\Delta H^0_T = 14659.45 + 10.573 \cdot T - 3.6315 \times 10^{-3} \cdot T^2 + 1.169 \times 10^5 \cdot T^{-1}$$

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and we can compute ΔH^0_{1000} by substituting T for 1000:

$$\Delta H^0_{1000} = 21717.85\ cal \cdot mole^{-1}$$

1.6.5.5. Use the equations:

$$C_{P_{C(s)}} = 1.1 + 4.8 \times 10^{-3} \cdot T - 1.2 \times 10^{-6} \cdot T^2 \qquad \left(cal \cdot \deg^{-1} \cdot mole^{-1}\right)$$

$$C_{P_{O_2(g)}} = 6.26 + 2.746 \times 10^{-3} \cdot T - 0.770 \times 10^{-6} \cdot T^2 \qquad \left(cal \cdot \deg^{-1} \cdot mole^{-1}\right)$$

$$C_{P_{CO(g)}} = 6.60 + 1.20 \times 10^{-3} \cdot T \qquad \left(cal \cdot \deg^{-1} \cdot mole^{-1}\right)$$

for $\Delta T = 298 - 2500\ K$ to find the temperature range within the heat effect of the reaction: $C(s) + \frac{1}{2} \cdot O_2(g) = CO(g)$ does not depend on the temperature.

Solution

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \Delta\left(\frac{\partial H}{\partial T}\right)_P = \Delta C_P$$

Corresponding to the above equation, the condition under ΔH^0 does not depend on the temperature is expressed by the equation: $\Delta C_P = 0$

$$\Delta C_P = C_{P_{CO}} - C_{P_C} - \frac{1}{2} \cdot C_{P_{O_2}} = 2.37 - 4.973 \times 10^{-3} \cdot T + 1.585 \times 10^{-6} \cdot T^2$$

If $\Delta C_P = 0 \Rightarrow 1.585 \times 10^{-6} \cdot T^2 - 4.973 \times 10^{-3} \cdot T + 2.37 = 0$

Solving the above equation we obtain two values for the temperature:

$T_1 = 586\ K$, and $T_2 = 2551.5\ K$. The value T_2 is not a valid value because is greater than 2500 *K*. Since the terms of the equation $\Delta C_P = \varphi(T)$ containing T are negative, than at T>586 *K* we have $\Delta C_P < 0$, i.e. at this temperature ΔH^0 passes through a minimum.

1.6.5.6. On the basis of the following data calculate the enthalpy of fusion of ice in $cal \cdot mole^{-1}$ at 10^0C: $C_{P,H_2O(s)} = 9.0\ cal \cdot mole^{-1} \cdot \deg^{-1}$ and $C_{P,H_2O(l)} = 18.0\ cal \cdot mole^{-1} \cdot \deg^{-1}$. ΔH for the fusion of ice at 0^0C is 1435 $cal \cdot mole^{-1}$.

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Solution

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_P dT = 1435 + (18-9)\cdot(T_2 - T_1) = 1435 + 9\cdot(263-273) \Rightarrow$$

$$\Delta H_{T_2} = 1345 \ cal \cdot mole^{-1}$$

1.6.5.7. Given the following data at 18^0C:

(1) $Fe(s) + 2\cdot HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$ $\quad \Delta H_1^0 = -21.0 \ kcal$

(2) $FeCl_2(s) + aq \rightarrow FeCl_2(aq)$ $\quad \Delta H_2^0 = -19.5 \ kcal$

(3) $HCl(g) + aq \rightarrow HCl(aq)$ $\quad \Delta H_3^0 = -17.5 \ kcal$

(4) $H_2(g) + Cl_2(g) \rightarrow 2\cdot HCl(g)$ $\quad \Delta H_4^0 = -44.0 \ kcal$

and heat capacities (in $cal \cdot mole^{-1} \cdot deg^{-1}$) for Fe (s), Cl_2 (g) and $FeCl_2$ (s) are 6.0, 8.2 and 18.5 respectively. For solid $FeCl_2$, find (a) ΔH^0 of formation at 18^0C; (b) ΔE^0 of formation at 18^0C; and (c) ΔH^0 of formation at 118^0C.

Solution

(a) $Fe(s) + Cl_2(g) \rightarrow FeCl_2(s)$

$$\Delta H_{291}^0 = \Delta H_1^0 - \Delta H_2^0 + 2\cdot\Delta H_3^0 + \Delta H_4^0 = -21.0 + 19.5 + 2\times 17.5 - 44.0 = -80.5 \ kcal$$

(b) $\Delta H_{291}^0 = \Delta E_{291}^0 + \Delta nRT \Rightarrow \Delta E_{291}^0 = \Delta H_{291}^0 - \Delta nRT = -80.5 + 1\times 1.987\times 10^{-3}\times 291$

$$\Delta E_{291}^0 = -79.91 \ kcal$$

(c) $\Delta C_P = 18.5 - 8.2 - 6.0 = 4.3 \ cal \cdot \deg^{-1}$

$$\Delta H_{391}^0 = \Delta H_{291}^0 + \Delta C_P \cdot (391 - 291) = -80.1 \ kcal$$

1.6.5.8. For the reaction: $H_2S(g) + \frac{3}{2}\cdot O_2(g) \rightarrow H_2O(g) + SO_2(g)$,

(a) Find ΔH^0 and ΔE^0 at 25^0C (use enthalpy values from appendices)

(b) Find ΔH^0 at 1000 K if:

$$\Delta C_P^0 = -2.162 + 5.634\times 10^{-3}\cdot T - 6.100\times 10^{-7}\cdot T^2 + 2.057\times 10^{-9}\cdot T^3 \ cal \cdot K^{-1}$$

(c) Do you have enough information to find ΔH^0 at 2000 K? Explain.

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Solution

(a) $\Delta H^0_{298} = -57.7979 - 70.96 - (-4.815) - 0 = -123.94\ kcal$

$$\Delta E^0_{298} = \Delta H^0_{298} - \Delta nRT = -123.94 - \left(-\frac{1}{2}\right) \times 1.987 \times 10^{-3} \times 298 = -123.64\ kcal$$

(b) $\Delta C^0_P = -2.162 + 5.634 \times 10^{-3} \cdot T - 6.100 \times 10^{-7} \cdot T^2 + 2.057 \times 10^{-9} \cdot T^3\ \ cal \cdot K^{-1}$

$$\Delta H^0_{1000} = \Delta H^0_{298} + \int_{298}^{1000} \Delta C^0_P dT = -123.94 - 2.162 \times 10^{-3} \times (1000 - 298) +$$
$$+ 2.817 \times 10^{-6} \times (1000^2 - 298^2) - 2.033 \times 10^{-10} \times (1000^3 - 298^3) +$$
$$+ 5.14 \times 10^{-13} \times (1000^4 - 298^4) = -122.58\ kcal$$

(c) The given data apply only to the range 298 to 1000 *K*. They tell us nothing about the behavior of the heat capacities above 1500 *K*. Therefore we cannot find ΔH^0 at 2000*K*.

1.6.5.9. For the reaction $3 \cdot A_2(g, 1\,atm) = 2 \cdot A_3(g, 1\,atm)$, $\Delta H^0_{300} = -35{,}000\ cal$. Making use of this fact and also the information given in the table below, derive a general expression of the form $\Delta H^0 = A + B \cdot T + C \cdot T^2 + D/T$ valid over the temperature range 300 to 500 *K* for the standard enthalpy of reaction as a function of temperature. Evaluate all constants numerically.

$$C^0_P\left(cal \cdot mole^{-1} \cdot K^{-1}\right) = a + b \cdot T + c/T^2$$

	a	$b \times 10^3$	$c \times 10^{-5}$	Range of validity
A_2 (g)	2.00	2.00	4.00	300 – 500 *K*
A_3 (g)	6.00	5.50	8.00	300 – 500 *K*

Solution

$$\Delta C^0_P\left(cal \cdot mole^{-1} \cdot K^{-1}\right) = 6.00 + 5.00 \times 10^{-3} \cdot T + 4.00 \times 10^5 \cdot \frac{1}{T^2}$$

$$\Delta H^0_{T_2} = \Delta H^0_{300} + \int_{300}^{T_2} 6.00 dT + \int_{300}^{T_2} 5.00 \times 10^{-3} \times T dT + \int_{300}^{T_2} \frac{4.00 \times 10^5}{T^2} dT \Rightarrow$$

$$\Delta H^0_{T_2} = -35{,}000 + 6.00 \times (T_2 - 300) + \frac{1}{2} \times 5.00 \times 10^{-3} \times (T_2^2 - 300^2) -$$

$$- 4.00 \times 10^5 \times \left(\frac{1}{T_2} - \frac{1}{300}\right) \Rightarrow$$

$$\Delta H^0_{T_2} = -35{,}692 + 6.00 \times T_2 + 2.50 \times 10^{-3} \times T_2^2 - 4.00 \times 10^5 \times \frac{1}{T_2}\ cal.mole^{-1}$$

$$\Delta H^0 = -35{,}692 + 6.00 \times T + 2.50 \times 10^{-3} \times T^2 - 4.00 \times 10^5 \times \frac{1}{T}\ cal.mole^{-1}$$

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1.6.5.10. Find ΔH^0 at 1000 K for the reaction $O_2(g) \rightarrow 2 \cdot O(g)$. $\Delta H^0_{298} = 117.04\ kcal$, $C_P(O) = \frac{5}{2} \cdot R$, if

$$\Delta C^0_P = 2 \times 4.968 - 6.148 - 3.102 \times 10^{-3} \cdot T + 9.23 \times 10^{-7} \cdot T^2 \ \ cal \cdot K^{-1}$$

Solution

For the given reaction:

$$\Delta H^0_{1000} = \Delta H^0_{298} + \int_{298}^{1000} \Delta C^0_P dT = 117{,}040 + 3.787 \times (1000 - 298) -$$

$$- \frac{1}{2} \times 3.102 \times 10^{-3} \times (1000^2 - 298^2) + \frac{1}{3} \times 9.23 \times 10^{-7} \times (1000^3 - 298^3) = 118.58\ kcal$$

1.6.5.11. Derive an equation for ΔH^0 of the following reaction as a function of temperature. The final equation must contain only T and numbers.

$A(s) + 2 \cdot B_2(g) \Leftrightarrow AB_4(g)$	$\Delta H^0_{300} = 500{,}000\ cal$
$C_P(A, s) = 5.00 + 3.00 \times 10^{-3} \cdot T$	$(cal \cdot mole^{-1} \cdot K^{-1})$
$C_P(B_2, g) = 6.00 + 4.00 \times 10^{-3} \cdot T$	$(cal \cdot mole^{-1} \cdot K^{-1})$
$C_P(AB_4, g) = 7.00 + 5.00 \times 10^{-3} \cdot T$	$(cal \cdot mole^{-1} \cdot K^{-1})$

Solution

$$\Delta C_P = C_P(AB_4) - C_P(A) - 2 \cdot C_P(B_2) = -10.00 - 6.00 \times 10^{-3} \cdot T$$

$$\Delta H_T = \Delta H_{300} + \int_{300}^{T} \Delta C_P dT = 500{,}000 + \int_{300}^{T} (-10.00 - 6.00 \times 10^{-3} \cdot T) dT =$$

$$= 500{,}000 - 10.00 \times (T - 300) - \frac{6.00 \times 10^{-3}}{2} \times (T^2 - 300^2) \Rightarrow$$

$$\Delta H_T = 503{,}270 - 10.00 \cdot T - 3.00 \times 10^{-3} \cdot T^2$$

1.6.5.12. For the hypothetical reaction $2 \cdot A(g) \rightarrow A_2(g)$, $\Delta C_P = 1.00 + 2.00 \times 10^{-3} \cdot T \ (cal \cdot K^{-1})$ and $\Delta H^0_{298} = -5.000\ kcal$. Estimate the temperature at which $\Delta H^0 = 0$ for this reaction at constant pressure.

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Solution

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta C_P dT$$

$$0-(-5000)=\int_{298}^{T_2}\left(1.00+2.00\times10^{-3}\cdot T\right)dT=1.00\times(T_2-298)+1.00\times10^{-3}\times\left(T_2^2-298^2\right)$$

$$5000=-298+1.00\cdot T-89+1.00\times10^{-3}\cdot T^2\Rightarrow 0=1.00\times10^{-3}\cdot T^2+1.00\cdot T-5387$$

Solving for T and disregarding the negative root, we obtain $T=1880\ K$

1.6.5.13. Calculate the maximum possible temperature produced by a flame consisting initially of 1 part by volume of H_2 (g) and 5 parts by volume of air (20 volume percent O_2 (g) and 80 volume percent N_2 (g)), if the ignition temperature is 25^0C. What are you assuming about the given heat capacity expressions?

$$C_P = a + b\cdot T \quad \left(cal\cdot mole^{-1}\cdot K^{-1}\right)$$

	a	$b\times10^{-3}$
H_2 (g)	6.947	-0.200
O_2 (g)	6.095	3.253
N_2 (g)	6.449	1.413
H_2O (g)	7.219	2.374

Solution

The reaction is: $2H_2(g)+O_2(g)+4N_2(g)\rightarrow 2H_2O(g)+4N_2(g)$

$$\Delta H^0_{298}=2\times(-57{,}800)=-115{,}600\ cal$$

Thus, +115,600 cal go into heating up 2 moles of H_2O (g) and 4 moles of N_2 (g) from 298.2 K to the final temperature, T_2.

$$2\cdot C_P(H_2O,g)+4\cdot C_P(N_2,g)=40.234+10.400\times10^{-3}\cdot T$$

$$115{,}600=\int_{298.2}^{T_2}40.234dT+\int_{298.2}^{T_2}\left(10.400\times10^{-3}\cdot T\right)dT\Rightarrow$$

$$115{,}600=40.234\times(T_2-298.2)+\frac{10.400\times10^{-3}}{2}\times\left(T_2^2-298.2^2\right)$$

$$115{,}600=40.234\times T_2-11{,}996+5.200\times10^{-3}\times T_2^2-462\Rightarrow$$

$$5.200\times10^{-3}\times T_2^2+40.234\times T-128.058=0$$

Applying the quadratic formula we obtain, disregarding the negative root, T_2 = 2425 *K*. The result is valid only if the given expressions for C_P are correct over the range 298 to 2425 *K*. If they fail at the higher temperature within this range, the result is erroneous.

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1.6.5.14. Let us find the heat of the reaction: $Cu(s)+\frac{1}{2}\cdot O_2(g)=CuO(s)$ at 500 and 1000 *K*.

The heat of reaction at 298 *K* is $Q_{298}=-37{,}500\ cal$. The temperature dependence of the heat capacities, C_P, has the following form:

Substance	$C_P=f(T)$
Cu (s)	$5.44+1.46\times10^{-3}\cdot T$
O_2 (g)	$8.27+0.26\times10^{-3}\cdot T-1.88\times10^{5}/T^2$
CuO (s)	$10.87+3.58\times10^{-3}\cdot T-1.51\times10^{5}/T^2$

Solution

Let us write an expression for the sum of the heat capacities:

$$\sum_i \nu_i C_{P,i}=C_{P_{CuO}}-C_{P_{Cu}}-\frac{1}{2}\cdot C_{P_{O_2}}=1.30+1.99\times10^{-3}\cdot T-0.57\times10^{5}/T^2$$

Insertion of this expression in equation:

$Q_{T_2}=Q_{T_1}+\int_{T_1}^{T_2}\sum_i \nu_i C_{P,i}\,dT$ and integration yields to:

$$Q_T=-37{,}500+\int_{298}^{T}\left(1.30+1.99\times10^{-3}\cdot T-0.57\times10^{5}/T^2\right)dT\Rightarrow$$

$$Q_T=-38{,}170+1.30\cdot T+0.99\times10^{-3}\cdot T^2+0.57\times10^{5}/T$$

Whence for 500 and 1000 *K* we get: $Q_{500}=-37{,}159\ cal$ and $Q_{1000}=-35{,}823\ cal$

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2. APPLICATIONS OF THE SECOND LAW OF THERMODINAMICS

2.1. REVERSIBLE AND IRREVERSIBLE PROCESS

2.1.1. Is the chaotic motion of molecules in a gas a case of perpetual motion and hence a violation of the laws of thermodynamics? Explain.

Solution

No. There is nothing wrong with perpetual motion of the first kind as long as the moving object is not called on to do any work (against friction, for example). The moving molecules often lose energy by collision but they gain just as much by other collisions. Friction does not destroy energy but merely randomizes it. In the gas the motion is already as random as it can be. As for perpetual motion of the second kind (violating the second law), it would occur only if the random motion of the molecules (heat) were to be converted into orderly motion (work) with no other process occurring.

2.1.2. (a) Is the Joule-Thomson experiment reversible? Explain by describing how one could, or could not, restore the gas to its initial state by the same path.

(b) Is the entropy of the gas constant in the Joule-Thomson experiment? If not, express $(\partial S/\partial P)_H$ in terms of any or all the variables P, V, T, C_P and C_V.

Solution

(a) The process is irreversible. Restoration by the same path would mean that the gas would have to flow through the porous plug from the lower to the higher pressure---a manifest impossibility. The gas can be restored to its initial state but only by a different process involving different amounts of work and heat.

(b) $dH = T\,dS + V\,dP = 0$

$$\left(\frac{\partial S}{\partial P}\right)_H = -\frac{V}{T}$$

2.1.3. Two bodies at different temperatures are connected by a wire with infinitesimal thermal conductance so that heat flows infinitely slowly from the hot body to the cold body until they are at the same temperature. Is this process reversible? Explain briefly.

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Solution

The process is irreversible because (a) the process cannot be reversed along the same path-heat will not flow along the wire from a cold to a hot body, or (b) ΔS for the universe is positive for the process described, no less so because of its slowness. A reversible process is infinitely slow, but an infinitely slow process is not necessarily reversible.

2.1.4. A person who has a superficial acquaintance with thermodynamics consults you about the following difficulty: "For the reaction $2H_2 + O_2 = 2H_2O$, ΔS is negative as we can see in the tables of third-law entropies. Entropy has to increase in every process. Should we conclude that this reaction is impossible?" Explain what the incorrect assumption is, what the corresponding correct statement is, and the special conditions, if any, under which the original assumption and conclusion would become correct.

Solution

No. The entropy of an *isolated* system must increase in every process. If H_2 and O_2 react in an isolated system, the product will be greater than that of the starting materials. ΔS calculated from the tables of third-law entropies refers to a process in which the product is restored in the initial temperature of the reactants. This process is indeed impossible in an isolated system.

2.1.5. A person who has a superficial acquaintance with thermodynamics consults you about the following difficulty: "I thought that every spontaneous process is accompanied by an increase of entropy, but on calculating the entropy change for the freezing of 1 mole of super cooled water at –5 °C, which I know intuitively to be a spontaneous process, I obtain an entropy change of –5.04 cal $°K^{-1}mole^{-1}$ for the H_2O. Since this is a spontaneous process, why isn't the entropy change positive?" Explain what the incorrect assumption is, what the corresponding correct statement is, and the special conditions, if any, under which the original assumption and conclusion would become correct.

Solution

The incorrect assumption is that the entropy of the system (water) must increase for a spontaneous change.

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The correct criterion for spontaneity is that the entropy of the universe (system+ surroundings) must increase for the process. To consider surroundings let us imagine that the freezing of the supercooled water takes place in an oil bath so large that the temperature of the bath is not significantly affected by the process. Then the entropy change for the bath (that is, the surroundings) would be $\Delta S = Q_{rev}/T \cdot \Delta H$ at –5 °C can be calculated by the Kichhoff law to be 1316 cal $mole^{-1}$, so that $\Delta S_{bath}=1376/268=5.13$ cal $K^{-1}mole^{-1}$.

Therefore the entropy change for the universe is -5.04+5.14=+0.1 cal k^{-1} and we see that the process is indeed accompanied by an increase in entropy.

2.1.6. For an adiabatic process Q=0 and therefore Q/T=0/T=0. Why, then, is there an entropy increase ($\Delta S>0$) in an adiabatic expansion into a vacuum?

Solution

It is not true, in general, that $\Delta S = \frac{Q}{T}$

This is true only for a reversible isothermal process.

In general, $\Delta S = \int \frac{\delta Q_{rev}}{T}$. If the gas is expanded reversibly to the same final state, $\Delta S = \int \frac{\delta Q_{rev}}{T} > 0$ this reversible expansion cannot be adiabatic; if it were, the final state would not be the same as in the irreversible adiabatic expansion. The gas would finish by being too cold because it would have done more work in the irreversible expansion.

2.1.7. A solid is melted to liquid at its melting point, T_m by transferring irreversibly to it a quantity of heat Q. It is true that for this process $\Delta S = \frac{Q}{T_m}$? If it is true, why and under what assumptions is justified in ignoring the fact that process is irreversible? If it is false, how can a correct expression for ΔS be obtained?

Solution

For any isothermal process $\Delta S = \frac{Q_{rev}}{T}$, where Q_{rev} is the heat absorbed when system is taken from the initial state to final state by a reversible path. We must ask then whether

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$Q=Q_{rev}$ for the process described here. Certainly $\Delta E = \Delta E_{rev}$, and $Q= \Delta E - W$. The question thus becomes does $W = W_{rev}$?

In the present case we are justified to assume that $W=W_{rev}$; for a melting process there is no work in any case and W_{rev}-W would be negligible than W. The only difference would result from expansion (or contraction) so rapid that the atmosphere could not keep up with it that means a thoroughly insignificant effect.

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2.2. THE ENTROPY IN CYCLIC PROCESSES

2.2.1. One mole of an ideal monoatomic gas ($C_V = 3/2R$) passes through the following reversible cyclic process (process A): (i) The gas is compressed adiabatically from pressure P_1 and temperature T_1 to pressure P_2 and temperature T_2; (ii) The gas is expanded isothermally from P_2 and T_2 to the initial pressure P_1; (iii) The gas is cooled isobarically (constant P) to the initial temperature T_1.

(a) Express P_2 in terms of P_1, T_1, T_2 and (if necessary) R.

(b) Find Q, W, ΔE, and ΔS for the gas in each of the three steps (i), (ii), and (iii), and in the entire process in terms of any or all of the quantities P_1, T_1, T_2 and R.

(c) In process B steps (i) and (iii) are the same as the corresponding steps in process A, but step (ii) is carried out irreversibly by allowing the gas to expand into a vacuum to attain the same final conditions P_1 and T_2. Find Q, W, ΔE, and ΔS for the gas in step (ii) of process B and in the entire process.

Solution

(a) $C_V = \frac{3}{2}R,\ C_P = \frac{5}{2}R$

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{T_2}{T_1}\right)^{C_P/R} = \left(\frac{T_2}{T_1}\right)^{5/2}$$

	Q	W	ΔH	ΔS
(b)				
(i)	0	$-\frac{3}{2}(T_2 - T_1)$	$-\frac{5}{2}R(T_2 - T_1)$	0
(ii)	$RT_2 \ln\frac{P_2}{P_1} = \frac{5}{2}RT_2 \ln\frac{T_2}{T_1}$	$RT_2 \ln\frac{P_2}{P_1} = \frac{5}{2}RT_2 \ln\frac{T_2}{T_1}$	0	$R\ln\frac{P_2}{P_1} = \frac{5}{2}R\ln\frac{T_2}{T_1}$
(iii)	$\frac{5}{2}R(T_1 - T_2)$	$R(T_1 - T_2)$	$\frac{3}{2}R(T_1 - T_2)$	$\frac{5}{2}R\ln\frac{T_1}{T_2}$
Total	$\frac{5}{2}R[\ (T_1 - T_2) + T_2 \ln\frac{T_1}{T_2}\ ]$	$\frac{5}{2}R[\ (T_1 - T_2) + T_2 \ln\frac{T_1}{T_2}\ ]$	0	0

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	Q	W	ΔH	ΔS
(c)				
(ii)	0	0	0	$\frac{5}{2}R\ln\frac{T_2}{T_1}$
Total	$\frac{5}{2}R(T_1-T_2)$	$\frac{5}{2}R(T_1-T_2)$	0	0

2.2.2. Make a rough sketch of the following cycle on a T-S diagram:

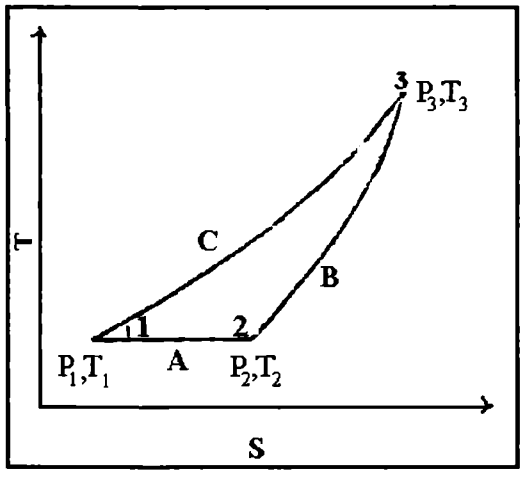
Step A. Isothermal expansion (at T_1) from P_1 to P_2.

Step B. Isochoric heating from P_2, T_1 to P_3, T_3.

Step C. Isobaric cooling from P_3, T_3 to P_1, T_1.

Solution

See figure. The steps in the cycle are labeled A, B, C.



Step A. Straightline, parallel to the S axis.

Step B. $dS_V = \frac{dE}{T} = \frac{(C_V dT)}{T}$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$$

$(\partial T/\partial S)_v$ gives the slope of the curve.

Step C. $dS_P = \frac{dH}{T} = \frac{(C_P dT)}{T}$

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$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}; \quad \left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P}$$

$(\partial T / \partial S)_P$ gives the slope of the curve.

2.2.3. Calculate the maximum theoretical efficiency of a reversible heat engine operating between 25° C and 100 °C.

Solution

$$\eta = \frac{W}{Q_2} = \frac{T_2 - T_1}{T_2} = \frac{373 - 298}{373} = 0.021$$

or 20.1 percent.

2.2.4. The efficiency of a refrigerator cycle is defined in terms of its coefficient of preformance,

$$\eta = \frac{Q_1}{W} \leq \frac{T_1}{T_2 - T_1}$$

where T_1 and T_2 are the temperatures of the cold box and the surroundings, Q_1 is the amount of heat withdrawn from the cold box, and $-W$ is the work required.

(a) Calculate the maximum η for a refrigerator that operates between 25 °C and -5°C.

(b) Calculate the minimun amount of work that must be done by the motor to withdraw 1 calorie of heat from the cold box at –5 °C and release it to the room at 25 °C.

Solution

$$\eta_{max} = \frac{T_1}{T_2 - T_1} = \frac{268.2}{298.2 - 268.2} = 8.94$$

$$-W_{min} = \frac{T_2 - T_1}{T_2} Q_1 = \frac{298.2 - 268.2}{268.2} \times 1cal = \frac{30.0}{268.2} = 0.112cal$$

2.2.5. A heat pump is essentially a refrigerator operated in revers; that is, it is used to heat the system at a higher temperature T_2 by cooling (pumping heat from) the surroundings at a lower temperature. Thus a heat pump could be used to warm a house by pumping heat from the cold outdoors and delivering it to the warm interior of the house. The

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advantage of this method over conventional methods of heating is that the maximum efficiency of a refrigerator is so much greater than that of other methods of heating. Consider, for example, a heat pump with a coefficient of performance

$$\eta = \frac{-Q_1}{W} = \frac{T_1}{T_2 - T_1} = 7.0$$

where Q_1 is the amount of heat absorbed at the lower temperature. Calculate Q_2/W the ratio of the heat liberated at the higher temperature to the work done.

Solution

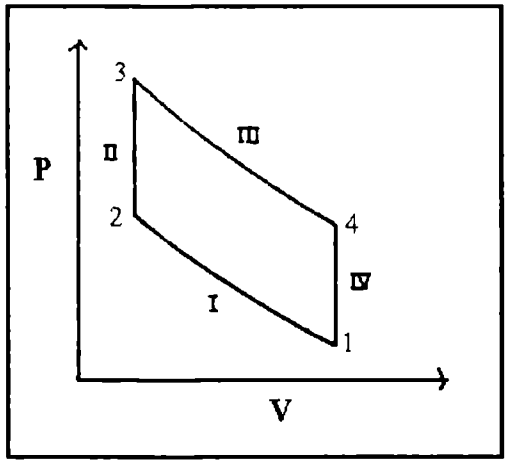
$$\eta = \frac{-Q_1}{W} = \frac{T_1}{T_2 - T_1} = 7.0 : \quad W = Q_1 + Q_2 : \quad Q_1 = W - Q_2 : \quad \frac{Q_2 - W}{W} = 7.0 :$$

$$\frac{Q_2}{W} = 8.0$$

Thus this heat pump would produce 8 times as much heat as a 100 percent efficient resistor per calorie of energy input.

2.2.6. The four stages of the Otto cycle are (see figure) I: isentropic compression, II: isochoric heat addition, III: isentropic expansion, IV: isochoric heat rejection. Show that the efficiency of a reversible Otto cycle with 1 mole of an ideal gas as the working substances W given by

$$\eta = 1 - r^{(1-\gamma)}$$



where $\gamma = C_P/C_V$ and r is the compression ratio (the ratio of the initial volume to the final volume for the compression process). What effect would have an increase in the compression ratio have on the efficiency of the cycle?

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Solution

I. $dS = 0$; $\delta Q = 0$ (rev); or $Q_I = 0$

$W_I = -\Delta E_I = -C_I(T_2 - T_1)$

II. $dV = 0$; $W_{II} = 0$; $Q_H = \Delta E_{II} = C_V(T_2 - T_1)$ (heat in)

III. $dS = 0$; $Q = 0$ (rev); $W_{III} = -\Delta E_{II} = -C_P(T_4 - T_3)$

IV. $dV = 0$; $W = 0$; $Q_{IV} = \Delta E_{IV} = -C_V(T_1 - T_4)$

$$\eta = \frac{W_{net}}{Q_{in}} = \frac{-C_V(T_2 - T_1) - C_V(T_4 - T_3)}{C_V(T_3 - T_2)} = \frac{-T_2 + T_1 - T_4 + T_3}{T_3 - T_2} = \frac{(T_3 - T_2) + (T_1 - T_4)}{T_3 - T_2}$$

$$= 1 + \frac{T_1 - T_4}{T_3 - T_2}$$

Since $dS_I = 0$, $S_I = S_2$; since $dS_{III} = 0$, $S_3 = S_4$.

Therefore

$S_3 - S_2 = S_4 - S_1$

Therefore

$$\int_{T_2}^{T_3} \frac{C_V dT}{T} = \int_{T_1}^{T_4} \frac{C_V dT}{T}$$

$$C_V \ln \frac{T_3}{T_2} = C_V \ln \frac{T_4}{T_1}$$

$$\frac{T_3}{T_2} = \frac{T_4}{T_1}; \text{ or } T_4 = \frac{T_1 T_3}{T_2}$$

$$\frac{T_1 - T_4}{T_3 - T_2} = \frac{-(T_1 T_3 / T_2) + T_1}{T_3 - T_2} = \frac{T_1(-T_3/T_2 + 1)}{T_3 - T_2} = \frac{T_1(T_2 - T_3)/T_2}{T_3 - T_2} = -\frac{T_1}{T_2}$$

$$\eta = 1 - \frac{T_1}{T_2}$$

For a reversible isentropic process $\delta Q = 0$ and $dE = -\delta W$

$C_V dT = -PdV$; $C_V dT = -RT\frac{dV}{V}$; $\frac{C_V dT}{T} = -\frac{RdV}{V}$

$$\frac{C_V}{R} \ln \frac{T_2}{T_1} = -\ln \frac{V_2}{V_1}; \quad \frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{R/C_V}; \quad \frac{R}{C_V} = \frac{C_P - C_V}{C_V} = \frac{C_P}{C_V} - 1 = \gamma - 1$$

$$\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma - 1} = 1 - \left(\frac{1}{r}\right)^{\gamma - 1}$$

$$\eta = 1 - r^{1-\gamma}$$

Since $C_P > C_V$, $\gamma > 1$ and $(1-r) < 0$; as r increase η decrease.

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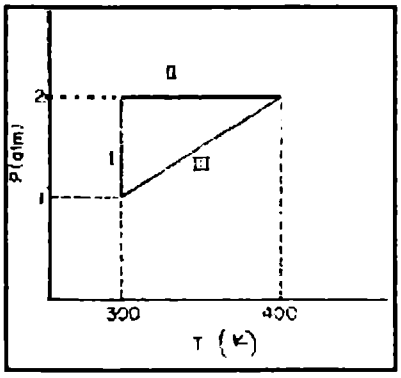
2.2.7. Two moles of an ideal monoatomic gas initially at 1 atm and 300 ° K are put through the following cycle, all stages of which are reversible; (I) isothermal compression to 2 atm, (II) isobaric tempersture increase to 400 °K, (III) return to the initial state by the path P = a + bT, where a and b are constants. Sketch the cycle on a P-T plot and evaluate numerically ΔE and ΔS for the working substance for each stage of the cycle.

Solution

The process is represented in figure.



$$\Delta E_I = \int_{300}^{300} nC_V dT = 0$$

$$\Delta E_{II} = \int_{300}^{400} nC_V dT = 2 \times \frac{3}{2} \times 1.99(400 - 300) = 597 cal$$

$$\Delta E_{III} = \int_{400}^{300} nC_V dT = 2 \times \frac{3}{2} \times 1.99(300 - 400) = -597 cal$$

$$dS_I = \frac{\delta w + dE}{T} = P\frac{dV}{T} + \frac{nC_V dT}{T} = \frac{nRTdV}{TV} + \frac{nC_V dT}{T}$$

$$\Delta S_I = nR \ln \frac{V_2}{V_1} + nC_V \ln \frac{T_2}{T_1} = 2 \times 1.99 \times 2.303 \log \frac{1}{2} + 0$$

$$= -2 \times 1.99 \times 2.303 \times 0.3010 = -2.76 cal \cdot K^{-1}$$

$$\Delta S_{II} = nR \ln \frac{V_2}{V_1} + nC_V \ln \frac{T_2}{T_1} = 2 \times 1.99 \times 2.303 \log \frac{400}{300}$$

$$+ 2 \times \frac{3}{2} \times 1.99 \times 2.303 \log \frac{400}{300} = 2.86 cal \cdot K^{-1}$$

$$\Delta S_I + \Delta S_{II} + \Delta S_{III} = 0$$

$$\Delta S_{III} = -\Delta S_I - \Delta S_{II} = 2.76 - 2.86 = -0.10 cal \cdot K^{-1}$$

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2.3. METHODS OF ENTROPY CALCULATION

2.3.1. IN PHASE TRANSITION

2.3.1.1. $\Delta S = \Delta H/T$ for which one of the following cases:

(a) A process for which $\Delta n_{gas} = 0$?

(b) A process for which $\Delta C_P = 0$?

(c) A process at constant pressure?

(d) An adiabatic process?

(e) An isothermal, reversible phase transition?

Solution

The right answer is (e).

2.3.1.2. The specific heat of fusion of benzene is 29.92 cal g^{-1}, its melting point $t_f = 5.5^0$C. Calculate the entropy of fusion of 1 g of benzene.

Solution

$$\Delta^{fus}S = \frac{29.92}{278.65} = 0.107 \text{ cal g}^{-1} \text{ deg}^{-1}$$

2.3.1.3. ΔH of fusion of H_2O at 0^0C = 1436 cal $mole^{-1}$, the values of C_P for the solid and liquid are 8.9 and 18.0 cal deg^{-1} $mole^{-1}$, respectively. Calculate (a) ΔH and (b) ΔS for the process H_2O (s, -10^0C) $\rightarrow$ H_2O (l, -10^0C) at constant pressure, 1 atm.

Solution

$$\Delta C_P = C_{P_l} - C_{P_s} = 9.1 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

(a) $$\Delta H_{263} = \Delta H_{273} + \int_{273}^{263} \Delta C_P dT = 1436 + 9.1(-10) = 1345 \text{ cal mole}^{-1}$$

(b) $$\Delta S_{263} = \Delta S_{273} + \int_{273}^{263} \frac{\Delta C_P}{T} dT = \frac{1436}{273} + 9.1 \ln \frac{263}{273} = 5.25 - 0.34 = 4.91 \text{ cal K}^{-1} \text{ mole}^{-1}$$

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2.3.1.4. The normal boiling point of benzene is 80.1^0C. Estimate the molar heat of vaporization of benzene at this temperature.

Solution

Trouton's rule: $\Delta H_v / T_b \approx 21$ cal deg^{-1} mole^{-1}

$\Delta H_v \approx T_b \times 21 = 353 \times 21 = 7400$ cal mole^{-1}

The experimental value is 7220 cal mole^{-1}.

2.3.1.5. One gram of liquid water at 100^0C is initially at 1.00 atm pressure and is confined to a volume in which no vapor is present. A valve is opened and water evaporates into an evacuated space of such volume that the final pressure is 0.10 atm. The entire apparatus is in a heat reservoir at 100^0C. ΔH for vaporization of H_2O is 540 cal g^{-1} at 100^0C. Assume that the vapor is an ideal gas and that the volume of the liquid is negligible as compared to volume of the vapor. Find Q and ΔS for (a) the water, (b) the reservoir, and (c) the universe. (d) Describe a reversible process by which the water could be brought to the same final state. Show in what way the final state of the universe after this reversible process would differ from its state after the actual process.

Solution

(a)Constant total volume:

W = 0

$Q_W = \Delta E = \Delta H - \Delta(PV) = \Delta H - RT\,(\Delta n_{gas})$

$$= 540 - 1.987 \times 373 \times \frac{1}{18.02} = 499 \text{ cal}$$

For ΔS construct a two-step process in which the initial and final states of the water are the same as in the given process:

Vaporization to gas at 1 atm:

$$\Delta S = \frac{\Delta H}{T} = \frac{540 cal/g}{373 K} = 1.448 \text{ cal K}^{-1} \text{ g}^{-1}$$

Expansion from 1 atm to 0.10 atm:

$$\Delta S = nRT \ln \frac{P_1}{P_2} = \frac{1}{18.02} \times 1.987 \ln 10 = 0.254 \text{ cal K}^{-1} \text{ g}^{-1}$$

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Total: $\Delta S_W = 1.702$ cal K^{-1}

(b) $Q_r = - Q_W = - 499$ cal,

$$\Delta S_r = \frac{-499cal}{373K} = -1.337 \text{ cal } K^{-1}$$

(For the reservoir, $W = 0$ and $\Delta E = Q$. The change in the state of reservoir, determined only by its content is the same whether a given of heat is withdraw reversibly or irreversibly. Therefore $\Delta S = Q/T_r$ even though the process described is irreversible).

(c) $Q_W = 0$, $\Delta S = 1.702 - 1.337 = 0.365$ cal K^{-1}

(d) (I) The water is allowed to evaporate reversibly against a constant opposing pressure at 1 atm.

(II) The water is allowed to evaporate reversibly against an opposing pressure equal to its own pressure.

Both steps are isothermal at 100^0C. In the reversible process the evaporating and expanding water does work in for example, lifting a weight, and this work is stored in the surroundings available for use in the reverse process if desired. In the irreversible process the water did no work and the possibility of obtaining work from it has been lost. Correspondingly less heat was withdrawn from the reservoir in the irreversible process.

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2.3.2. IN HEATING OR EXPANDING PROCESSES UNDER DIFFERENT CIRCUMSTANCES

2.3.2.1. Write a mathematical expression for the entropy change taking place in the working substance under each of the following circumstances:

(a) Free expansion of 1 mole of an ideal gas from V_1 to V_2;

(b) Reversible, isothermal phase transition;

(c) Reversible, adiabatic expansion of 1 mole of an ideal gas from V_1 to V_2;

(d) Reversible, isothermal expansion of 1 mole of an ideal gas from V_1 to V_2.

Solution

(a) $dS = \frac{\delta Q_{rev}}{T} = \frac{dE - \delta W}{T}$; $dE = 0$

$$\Delta S = \int_{V_1}^{V_2} \frac{PdV}{T} = \int_{V_1}^{V_2} \frac{nRTdV}{VT} = nR \ln \frac{V_2}{V_1}$$

(b) $\Delta S = \frac{\Delta^{tr} H}{T}$

(c) $\Delta S = 0$

(d) $dS = \frac{dE - \delta W}{T}$; $dE = 0$;

$$\Delta S = \int_{V_1}^{V_2} \frac{PdV}{T} = \int_{V_1}^{V_2} \frac{nRTdV}{VT} = nR \ln \frac{V_2}{V_1}$$

2.3.2.2. Calculate the change in the entropy of one gram-atom of aluminium when heated from 25 to 600^{0}C. The true atomic heat capacity of aluminium can be expressed by the equation:

$C_P = 5.006 + 0.002564T$ (cal mole^{-1} K^{-1})

Solution

$$\Delta S = \int_{298}^{873} \frac{C_p}{T} dT = 5.006 \times 2.303 \lg \frac{873}{298} + 0.002564(873 - 298)$$

$$= 5.38 + 1.47 = 6.85 \text{ cal mole}^{-1} \text{ K}^{-1}$$

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2.3.2.3. Calculate (a) ΔS, (b) ΔH, (c) ΔE for the process

1 mole H_2O (l, 20^0C, 1 atm) $\rightarrow$ 1 mole H_2O (g, 250^0C, 1 atm)

given the following data:

$C_P(l) = 18.0$ cal deg^{-1} mole^{-1}

$C_P(g) = 8.6$ cal deg^{-1} mole^{-1}

ΔH for vaporisation of H_2O at 100^0C and 1 atm = 9720 cal mole^{-1}

Solution

Resolve the process into the following steps:

(i) Heat from 20^0 to 100^0C:

$$\Delta H = C_P(T_2 - T_1) = 18.0(80) = 1440 \text{ cal mole}^{-1}$$

$$\Delta S = C_P \ln\frac{T_2}{T_1} = 18.0 \ln\frac{373.15}{293.15} = 4.35 \text{ cal K}^{-1} \text{ mole}^{-1}$$

(ii) Vaporize at 100^0C:

$$\Delta H = 9720 \text{ cal mole}^{-1}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{9720 - 0}{373.15} = 26.02 \text{ cal K}^{-1} \text{ mole}^{-1}$$

(iii) Heat from 100^0 to 250^0C:

$$\Delta H = C_P(T_2 - T_1) = 8.6(150) = 1290 \text{ cal mole}^{-1}$$

$$\Delta S = C_P \ln\frac{T_2}{T_1} = 8.6 \ln\frac{523.15}{373.15} = 2.91 \text{ cal K}^{-1} \text{ mole}^{-1}$$

(a) $\Delta S = 4.35 + 26.02 + 2.91 = 33.28$ cal K^{-1} mole^{-1}

(b) $\Delta H = 1440 + 9720 + 1290 = 12{,}450$ cal mole^{-1}

(c) $\Delta E = \Delta H - \Delta(PV) = \Delta H - P\Delta V$

$$\Delta V = V_{g,523} - V_{l,293} \approx V_{g,523}$$

if we make the approximation that the volume of the liquid is negligible in comparison to the volume of the gas.

$$P\Delta V = PV_{g,523} = RT = 1.987 \frac{cal}{\text{deg}.mole} \times 523.15^0 = 1040 \text{ cal mole}^{-1}$$

if we assume that the gas is ideal.

$\Delta E = 12{,}450 - 1{,}040 = 11{,}410$ cal mole^{-1}

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2.3.2.4. 200 g of tin [heat capacity 6.1 cal $(g\ atom)^{-1}$] initially at 100.0^0C and 100 g of water (heat capacity 18.0 cal $mole^{-1}$) initially at 25.0^0C are mixed together in a calorimeter. Assuming that the heat capacities are constant and that no heat is lost or gained by the surroundings or by the calorimeter itself, what is (a) the final temperature of the system, and (b) entropy change for (i) the tin, (ii) the water, and (iii) the universe?

Solution

(a) Let t_f = the final temperature

$Q_{tin} = Q_{water}$

$$\frac{100}{18.0}\times 18.0\times(t_f - 25) = \frac{200}{118.7}\times 6.1(100 - t_f)$$

$t_f = 31.9\ ^0$C

(b) $$\Delta S_{water} = \int_{298.2}^{330.1}\frac{nC_p dT}{T} = \frac{100}{18.0}\times 18.0\times 2.303\log\frac{330.1}{298.2} = 10.21\ \text{cal deg}^{-1}$$

$$\Delta S_{tin} = \int_{298.2}^{330.1}\frac{nC_p dT}{T} = \frac{200}{118.7}\times 6.1\times 2.303\log\frac{330.1}{298.2} = -1.26\ \text{cal deg}^{-1}$$

$\Delta S_{universe} = \Delta S_{water} + \Delta S_{tin} = 10.21 - 1.26 = 8.95$ cal K^{-1}

2.3.2.5. Evaluate ΔS for the isothermal, reversible expansion, at temperature T, from volume V_1 to V_2 of 1 mole of a gas that has the equation of state $PV = RT + A$. You may assume that $\Delta E = 0$ for this process.

Solution

$\delta Q = dE - \delta W;\quad dE = 0;\quad \delta Q = -\delta W = PdV$

$$\Delta S = \int_{V_1}^{V_2}\frac{PdV}{T} = \int_{V_1}^{V_2}\frac{(RT + A)dV}{TV}$$

$$\Delta S = (R + \frac{A}{T})\ln\frac{V_2}{V_1}$$

2.3.2.6. Two samples (1 and 2), 1 mole each, of the same ideal gas occupy equal volumes V and are initially at temperature T_1 and T_2 with $T_2 > T_1$. The molar heat capacity C_v is independent of temperature. The two containers are placed in contact through a heat-conducting but gas-impervious wall and the gases are allowed to come to the same temperature T_3, their volumes remaining constant. There is no leakage of heat except

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between the two gases. The containers have negligible heat capacities. Call this process A.

(a) Find T_3 in terms of given quantities.

(b) Devise a reversible process (process B) by which the gases can be transferred from the initial state to the same final state. (There are at least two simple ways in which the temperature of a gas can be changed reversibly).

(c) Find ΔS for each gas sample, for the surroundings and for the universe in each step of process B and in the entire process.

Solution

(a) The heat gained by 1 is equal to the heat lost by 2:

$$C_V(T_3 - T_1) = C_V(T_2 - T_3), \qquad T_3 = \frac{(T_1 + T_2)}{2}$$

(b) The following process is one of several possibilities: Let gas 1 be compressed and gas 2 expanded, adiabatically and reversibly, so that each has the final temperature T_3. To find their volumes (V_1 and V_2) we use the equation PV^γ = constant = $RTV^{\gamma-1}$, where $\gamma = C_p / C_V = (C_V + R)/C_V$.

For gas 1

$$T_1 V^{\gamma-1} = T_3 V_1^{\gamma-1}, \qquad \frac{V_1}{V} = \left(\frac{T_1}{T_3}\right)^{1/(\gamma-1)}$$

For gas 2

$$T_2 V^{\gamma-1} = T_3 V_2^{\gamma-1}, \qquad \frac{V_2}{V} = \left(\frac{T_2}{T_3}\right)^{1/(\gamma-1)}$$

We now expand gas 1 from V_1 to V and compress gas 2 from V_2 to V, isothermally and reversibly, keeping them in contact with a heat reservoir at the temperature T_3.

(c) In the adiabatic steps there are no entropy changes. In the isothermal steps we have

$$\Delta S_{gas1} = R \ln \frac{V}{V_1} = \frac{R}{\gamma - 1} \ln \frac{T_3}{T_1} = C_V \ln \frac{T_3}{T_1}$$

$$\Delta S_{gas2} = R \ln \frac{V}{V_2} = C_V \ln \frac{T_3}{T_2}$$

The heat emitted (or absorbed) by the gas or absorbed (or emitted) by the universe at the same temperature T_3:

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$$\Delta S_{surroundings} = -(\Delta S_{g1} + \Delta S_{g2}) = -C_V \ln\frac{T_3^2}{T_1 T_2} = C_V \ln\frac{4T_1T_2}{(T_1+T_2)^2}$$

$$\Delta S_{universe} = 0$$

2.3.2.7. Show that: (a) $(\partial V/\partial S)_P = (\partial T/\partial P)_S$; (b) Find $(\partial V/\partial S)_P$ for an ideal gas in terms of T, P, C_P and universal constants.

Solution

(a) $TdS = dH - VdP;\ dH = TdS + VdP$

We suppose $H = H(S,P)$ and because dH is an exact differential

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

$$dH \equiv dH$$

that means:

$$\left(\frac{\partial H}{\partial S}\right)_P = T \text{ and } \left(\frac{\partial H}{\partial P}\right)_S = V$$

and we proced:

$$\left(\frac{\partial^2 H}{\partial S \partial P}\right) = \left(\frac{\partial T}{\partial P}\right)_S \text{ and } \left(\frac{\partial^2 H}{\partial P \partial S}\right) = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$$

(b) $$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S = -\frac{(\partial S/\partial P)_T}{(\partial S/\partial T)_P}$$

$$\left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P dT + \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right] dP$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T};\ \left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T}\left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]$$

For an ideal gas $\left(\frac{\partial H}{\partial P}\right)_T = 0$ and

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{V}{T} = -\frac{RT}{PT} = -\frac{R}{P}$$

and hence

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$$\left(\frac{\partial V}{\partial S}\right)_P = -\frac{-\frac{R}{P}}{\frac{C_P}{T}} = \frac{RT}{PC_P}$$

2.3.2.8. (a) Show that for a van der Waals gas

$$\left(\frac{\partial V}{\partial T}\right)_S = \frac{-C_V(V-b)}{RT}$$

(b) Obtain an equation relating the initial and final temperatures to the initial and final volumes in a reversible adiabatic expansion of a van der Waals gas, preferably by using the result of (a). Assume that C_V is independent of T and V .

Solution

a) $$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{(\partial S/\partial T)_V}{(\partial S/\partial V)_T} = -\frac{C_V}{T(\partial P/\partial T)_V}$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2}; \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}; \quad \left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V(V-b)}{RT}$$

b) S is constant is this process. Then

$$dV = \left(\frac{\partial V}{\partial T}\right)_S dT; \quad \frac{dV}{V-b} = -\frac{C_V dT}{RT}$$

$$\ln\left(\frac{V_2-b}{V_1-b}\right) = -\frac{C_V}{R}\ln\left(\frac{T_2}{T_1}\right)$$

2.3.2.9. Calculate the entropy change involved in expanding 2 moles of hydrogen from 30 liters at 2 atmospheres pressure to 100 liters at 1 atmosphere pressure.
Assume C_p to be 7.4 cal K^{-1} and at these pressure hydrogen behaves ideal.

Solution

$$\begin{cases} V_1 = 30l \\ P_1 = 2atm \\ n_1 = 2mole \end{cases} \Rightarrow P_1V_1 = n_1RT_1 \Rightarrow T_1 = \frac{30\times 2}{2\times 0.082} = 365.85K$$

$$\begin{cases} V_2 = 100l \\ P_2 = 1atm \\ n_2 = n_1 = 2mole \end{cases} \Rightarrow P_2V_2 = n_2RT_2 \Rightarrow T_2 = \frac{100\times 1}{2\times 0.082} = 609.75K$$

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$$\Delta S = n\left(C_P \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}\right)$$

$$\Delta S = 2\left(7.4\ln\frac{609.75}{365.85} - 1.987\ln\frac{1}{2}\right) = 2(3.78 + 1.377) = 2\times 5.157 = 10.315\ \text{cal K}^{-1}$$

2.3.2.10. The Berthelot equation of state is

$$P = \frac{RT}{V-b} - \frac{a}{TV^2}$$

where a and b are constants characteristic of the gas. For a gas that is described by this equation, show that

(a) $\left(\frac{\partial S}{\partial V}\right)_T = \frac{R}{V-b} + \frac{a}{T^2V^2}$

(b) $\left(\frac{\partial E}{\partial V}\right)_T = \frac{2a}{TV^2}$

(c) $\left(\frac{\partial C_V}{\partial V}\right)_T = -\frac{2a}{T^2V^2}$

(d) $\left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V}{T}\left(\frac{R}{V-b} + \frac{a}{T^2V^2}\right)^{-1}$

(e) $\left(\frac{\partial V}{\partial T}\right)_P = \frac{-R/(V-b) - a/T^2V^2}{-RT/(V-b)^2 + 2a/TV^3}$

(f) $C_P - C_V = \frac{-T\left[R/(V-b) + a/T^2V^2\right]^2}{-RT/(V-b)^2 + 2a/TV^3}$

(g) For the special case in which $a = 0$ and C_V is independent of temperature obtain an equation that relates the initial and final volumes to the initial and final temperatures in a reversible adiabatic expansion of a Berthelot gas. Show how the result follows from one or more of the equations given in (a) – (f) above.

Solution

(a) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} + \frac{a}{T^2V^2}$

(b) $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = \frac{RT}{V-b} + \frac{a}{T\,V^2} - \frac{RT}{V-b} + \frac{a}{TV^2} = \frac{2a}{TV^2}$

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(c) $\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial^2 E}{\partial T \partial V} = -\frac{2a}{T^2V^2}$

(d) $\left(\frac{\partial V}{\partial T}\right)_S = -\frac{(\partial S/\partial T)_V}{(\partial S/\partial V)_T} = -\frac{C_V}{T}\left(\frac{R}{V-b} + \frac{a}{T^2V^2}\right)^{-1}$

(e) $\left(\frac{\partial V}{\partial T}\right)_P = -\frac{(\partial P/\partial T)_V}{(\partial P/\partial V)_T} = \frac{-R/(V-b) + a/T^2V^2}{-RT/(V-b)^2 + 2a/TV^3}$

(f) $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = \frac{-T\left[R(V-b) + a/T^2V^2\right]^2}{-RT/(V-b)^2 + 2a/TV^3}$

(g) In a reversible adiabatic process S is constant.

$$\frac{dV}{dT} = \left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V}{T}\left[\frac{R}{V-b} + \frac{a}{T^2V^3}\right]^{-1}$$

Here $a = 0$ and C_V is constant.

$$\frac{dV}{dT} = \frac{-C_V(V-b)}{RT}; \quad \frac{RdV}{V-b} = -\frac{C_V dT}{T}; \qquad R\ln\frac{V_2-b}{V_1-b} = -C_V \ln\frac{T_2}{T_1}$$

2.3.2.11. Using the equations $dE = T\,dS - P\,dV$ and $H = E + PV$, prove that

$$\left(\frac{\partial E}{\partial S}\right)_P = T - P\left(\frac{\partial T}{\partial P}\right)_S$$

Solution

$$dE = T\,dS - P\,dV \quad ; \quad \left(\frac{\partial E}{\partial S}\right)_P = T - P\left(\frac{\partial V}{\partial S}\right)_P$$

$dH = dE + V\,dP + P\,dV = T\,dS + V\,dP$

Therefore $(\partial V/\partial S)_P = (\partial T/\partial P)_S$ (see problem 2.3.2.7). Then

$$\left(\frac{\partial E}{\partial S}\right)_P = T - P\left(\frac{\partial T}{\partial P}\right)_S$$

2.3.2.12. Prove that: (a) $\left(\frac{\partial S}{\partial P}\right)_H = -\frac{V}{T}$ and (b) $\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_V}{TV\alpha} + \frac{\alpha}{\beta}$

Solution

(a)$dH = T\,dS + V\,dP$; $\left(\frac{\partial S}{\partial P}\right)_H = -\frac{V}{T}$

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(b) $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

$$\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial S}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial V}\right)_P = \left(\frac{\partial P}{\partial T}\right)_V + \frac{C_V}{T} \cdot \frac{1}{V\alpha}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = \frac{\alpha}{\beta} \text{ and } \left(\frac{\partial S}{\partial V}\right)_P = \frac{\alpha}{\beta} + \frac{C_V}{TV\alpha}$$

2.3.2.13. Prove each of the following relationships:

(a) $\left(\frac{\partial V}{\partial S}\right)_P = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P$ and (b) $\left(\frac{\partial T}{\partial P}\right)_H = T\left(\frac{\partial V}{\partial H}\right)_P - V\left(\frac{\partial T}{\partial H}\right)_P$

Solution

(a) $dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P$$

(b) $$\left(\frac{\partial V}{\partial H}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial H}\right)_P = \frac{1}{C_P}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{(\partial H/\partial P)_T}{(\partial H/\partial T)_P} = -\frac{1}{C_P}\left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] = -\frac{V}{C_P} + \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P = -V\left(\frac{\partial T}{\partial H}\right)_P + T\left(\frac{\partial V}{\partial H}\right)_P$$

2.3.2.14. For a gas which follows the equation of state $PV = RT - BP + APT$, show that

$$C_P - C_V = R\left(1 + \frac{AP}{R}\right)^2.$$

Solution

$$\delta Q = dE + PdV = \left(\frac{\partial E}{\partial T}\right)_V dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]dV = dH - VdP = \left(\frac{\partial H}{\partial T}\right)_P dT + \left[\left(\frac{\partial H}{\partial P}\right)_T - V\right]dP$$

but $V = V(T, P)$ and $dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$

hence

$$\delta Q = \left(\frac{\partial E}{\partial T}\right)_V dT + \left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]\left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right]$$

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$$= \left\{ \left(\frac{\partial E}{\partial T} \right)_V + \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] \cdot \left(\frac{\partial V}{\partial T} \right)_P dT \right\} + \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] \cdot \left(\frac{\partial V}{\partial P} \right)_T dP$$

We estimate $\left(\frac{\partial E}{\partial V} \right)_T$ from equation

$$dE = TdS - PdV; \quad \left(\frac{\partial E}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P = T \left(\frac{\partial P}{\partial T} \right)_V - P$$

and

$$\left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial E}{\partial T} \right)_V + \left[T \left(\frac{\partial P}{\partial T} \right)_V - P + P \right] \cdot \left(\frac{\partial V}{\partial T} \right)_P$$

$$C_P - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \cdot \left(\frac{\partial V}{\partial T} \right)_P$$

P from the equation of state is:

$$P(V + B - AT) = RT \text{ and } P = \frac{RT}{V - AT + B}$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{V - AT + B} + \frac{ART}{(V - AT + B)^2} = \frac{R(V + B)}{(V - AT + B)^2}$$

and $V = \frac{RT}{P} + AT - B; \quad \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P} + A$

and the difference

$$C_P - C_V = T \cdot \frac{R(V + b)}{(V - AT + B)^2} \cdot \left(\frac{R}{P} + A \right)$$

From the equation of state:

$$(V - AT - B)^2 = \left(\frac{RT}{P} \right)^2 \text{ and hence}$$

$$C_P - C_V = \frac{RT \left(\frac{RT}{P} + AT \right)}{\left(\frac{RT}{P} \right)^2} \left(\frac{R}{P} + A \right) = \frac{RT^2 \left(\frac{R}{P} + A \right)^2 \cdot P^2}{R^2 T^2} = \frac{P^2}{R} \left(\frac{R}{P} + A \right)^2 = R \left(1 + \frac{AP}{R} \right)^2$$

2.3.2.15. For a gas which respect the equation of state $P\ (V - b) = RT$, the heat capacity follows the equation $C_V = a + bT + cT^2$. Derive an expression for the entropy change of 1 mole of gas that accompanies a change in its state from T_i, P_i to T_f, P_f.

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Solution

$$dS = \frac{\delta Q_{rev}}{T} = \frac{dE - \delta W}{T} = \frac{C_v dT}{T} + \frac{PdV}{T}$$

We evaluate first $C_V \frac{dT}{T}$

$$\int_{T_i}^{T_f} \frac{C_V dT}{T} = \int_{T_i}^{T_f} \frac{adT}{T} + \int_{T_i}^{T_f} bdT + \int_{T_i}^{T_f} cTdT = a \ln \frac{T_f}{T_i} + b(T_f - T_i) + \frac{c}{2}(T_f^2 - T_i^2)$$

We evaluate $\frac{PdV}{T}$; from the equation of state $P = \frac{RT}{V-b}$ and $\frac{PdV}{T} = -\frac{R}{(V-b)^2} dV$.

$$\int_{V_i}^{V_f} \frac{PdV}{T} = R \ln \frac{V_f - b}{V_i - b} \text{ and}$$

$$\Delta S = a \ln \frac{T_f}{T_i} + b(T_f - T_i) + \frac{c}{2}(T_f^2 - T_i^2) + R \ln \frac{V_f - b}{V_i - b}$$

2.3.2.16. Estimate: (a) $(\partial C_V / \partial V)_T$; (b) $(\partial T / \partial V)_E$ and (c) $(\partial T / \partial V)_S$ for a van der Waals gas:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT.$$

One mole of this gas at the initial temperature T_1 is confined to a volume V_1. It is then allowed to expand adiabatically:

(d) into an evacuated space

(e)reversibly, so that its final volume in each case is V_2. Express its final temperature T_2 in terms of T_1, V_1, V_2, R, a and b for each process (d) and (e).

(f) Evaluate T_2 for each of the process (d) and (e) with T_1 = 300 K, V_1 = 1l, V_2 = 100 l, a = 10 l^2 atm mole^{-2} and b = 0.

Solution

(a) $dE = TdS - PdV$; $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$; $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

From van der Waals equation:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}; \quad \frac{dP}{dT} = \frac{R}{V-b} \text{ and } \left(\frac{\partial E}{\partial V}\right)_T = \frac{RT}{V-b} - P = \frac{RT}{V-b} - \frac{RT}{V-b} + \frac{a}{V^2} = \frac{a}{V^2}$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial^2 E}{\partial V \partial T} = \left[\frac{\partial}{\partial T}\left(\frac{a}{V^2}\right)\right]_V = 0$$

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(b) $dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV,\ E = ct.$

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{(\partial E/\partial V)_T}{(\partial E/\partial T)_V} = -\frac{a/V^2}{C_V} = -\frac{a}{C_V V^2}$$

(c) $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV,\ S = ct.$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_V} = -\frac{(\partial P/\partial T)_P}{C_V/T} = -\frac{RT}{C_V(V-b)}$$

Because this gas is a monoatomic one, $C_V = \frac{3}{2}R$ in the ideal limit of infinite volume;

and because of (a) C_V is independent of volume. Therefore $C_V = \frac{3}{2}R$ at all volumes.

(d) $W = 0$, $Q = 0$ and $\Delta E = 0$.

$dT = \left(\frac{\partial T}{\partial V}\right)_E \cdot dV$ and

$$T_2 = T_1 + \int_{V_1}^{V_2}\left(\frac{\partial T}{\partial V}\right)_E dV = T_1 - \frac{a}{C_V}\int_{V_1}^{V_2}\frac{dV}{V^2} = T_1 + \frac{2a}{3R}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

(e) in an adiabatic reversible process $\Delta S = 0$ and $dT = \left(\frac{\partial T}{\partial V}\right)_S dV = -\frac{RT}{C_V(V-b)}dV$

$$\frac{dT}{T} = -\frac{R}{C_V}\frac{dV}{V-b} \text{ and } \ln\frac{T_2}{T_1} = \frac{R}{C_V}\ln\frac{V_1-b}{V_2-b} = \frac{2}{3}\ln\frac{V_1-b}{V_2-b} \text{ or } T_2 = T_1\left(\frac{V_1-b}{V_2-b}\right)^{2/3}$$

(f) (d) $T_2 = 300 + \frac{2\times 10}{3\times 0.08206}\left(\frac{1}{100} - \frac{1}{1}\right) = 219.5K$

(e) $T_2 = 300\left(\frac{1}{100}\right)^{2/3} = 3\times 100^{1/3} = 13.9K$

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2.3.3. IN TRANSITION OF SUPERCOOLED LIQUID INTO THE SOLID STATE

2.3.3.1. Calculate the change in the entropy and reduced heat for a non-equilibrium process - the transition into ice of one mole of liquid water supercooled to $-5°C$ if $C_{pl} = 18$ cal deg^{-1} $mole^{-1}$, C_{ps}=9cal$deg^{-1}$$mole^{-1}$, $\Delta^{fus}H = 1438\ cal\ mole^{-1}$, $P^0_{l/-5^0C} = 3.156 mmHg$, $P^0_{s/-5^0C} = 3.008 mmHg$

Solution

The change in the entropy can be calculated as the sum of the reduced heats along an equilibrium path between these states. For the process under consideration the calculation can be carried out along two equilibrium paths, I and II.

I. The liquid water is heated from -5 to $0°C$ (1) then it reversibly solidifies (2), and, finally, the ice cools to $-5°C$ (3). The changes in the entropy for the three processes along this path are calculated by the methods set out you already know.

(1) $\Delta S_1 = C_{p,l} \ln \frac{T_2}{T_1} = 18 \times 2.303 \lg \frac{273.2}{268.2} = 0.334 cal\ \deg^{-1}\ mole^{-1}$

(2) $\Delta S_2 = -\frac{\Delta^{fus}H}{T_f} = -\frac{1438}{273.2} = -5.264 cal\ \deg^{-1}\ mole^{-1}$

(3) $\Delta S_3 = C_{p,s} \ln \frac{T_2}{T_1} = 9 \times 2.303 \lg \frac{268.2}{273.2} = -0.166\ cal\ \deg^{-1}\ mole^{-1}$

The total change in the entropy is

$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -5.096 cal\ \deg^{-1}\ mole^{-1}$

II The liquid water evaporates reversibly (under the pressure of its saturated vapor P_1 = 3.156 mm Hg) at $-5°C$ (1). Next the water vapor expands isothermally until the pressure becomes equal to P_2 = 3.008 mm Hg (the pressure of the saturated vapor of ice) (2). Finally, the vapor condensates into ice at $-5°C$ (3).

Solution

First we compute the value of the heat of solidification of water required for the calculation of change of state of water at $-5°C$. according to Kirchhoff's formula.

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$H_2O(l) \Leftrightarrow H_2O(s)$

$\Delta^S H(-5°C) = \Delta^S H(0°C) + \Delta C_p(t-t_0)$

$= -1438-9(-5) = -1393$ cal mole^{-1}

Then:

(1) $\Delta S_1 = \frac{\Delta^v H}{T_t} = \frac{\Delta^v H}{268.2}$

(2) $\Delta S_2 = R \ln \frac{p_1}{p_2} = 4.576 \lg \frac{3.156}{3.008} = 0.095$

(3) $\Delta S_3 = -\frac{\Delta^{sub} H}{T} = -\frac{\Delta^{sub} H}{268.2}$

Summation gives:

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = \frac{\Delta^v H - \Delta^{sub} H}{T_s} + 0.095$$

Since, then

$$\Delta S = -\frac{1393}{262.2} + 0.095 = -5.194 + 0.095 = -5.099 cal \deg^{-1} mole^{-1}$$

the values of ΔS found for one process carried out along two different equilibrium paths are equal to each other (the discrepancy equal 0.002 cal deg^{-1} mole^{-1} is due to the inevitable inaccuracy of the data used). This should be expected since entropy is a function of state.

The reduced heat received by the water in the irreversible process upon its direct solidification at -5°C is equal to:

$$\frac{Q}{T} = \frac{\Delta^s H}{T} = -\frac{1393}{268.2} = -5.194 cal \deg^{-1} mole^{-1}$$

A comparison of the quantities ΔS and $\frac{Q}{T}$ shows that the accordance with the equation

$\int_1^2 \left(\frac{\delta Q}{T}\right)_{noneq} < S_2 - S_1$, we have $\Delta S > \frac{Q}{T}$.

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2.3.4. IN MIXING OF TWO GASES

2.3.4.1. Calculate ΔS for mixing of 1 mole of nitrogen with three moles of oxygen at 25^0C and a final total pressure of 1 atm.

The initial pressure of each gas is 1 atm.

Solution:

$$\Delta S = -R(x_1 \ln x_1 + x_2 \ln x_2)$$

when x_1 = mole fraction of nitrogen and

x_2 = mole fraction of oxygen

$$\Delta S = -1.987 \times 2.303(0.25 \lg 0.25 + 0.75 \lg 0.75) = -4.576(-0.2442) = 1.12 \text{ cal deg}^{-1}$$

2.3.4.2. In 1 l chamber is confined hydrogen at 25^0C and P = 1 atm. This chamber is connected to another 2 l chamber containing oxygen at 25^0C and 0.5 atm. If the gases diffuse one into each other, at T = ct., what is the value of ΔS?

Suppose that gases are ideal.

Solution

$V_f = V_1 + V_2 = 3$ l

$$\Delta S = -n_1 R \ln \frac{V_1}{V_f} - n_2 R \ln \frac{V_2}{V_f}$$

$$n_1 = \frac{P_1 V_1}{RT} = \frac{1 atm \cdot 1l}{0.08206 \cdot l \cdot atm \cdot mole^{-1} \cdot K^{-1} \times 298K} = 0.0408 \text{ mole}$$

$$n_2 = \frac{P_2 V_2}{RT} = \frac{0.5 atm \cdot 2l}{0.08206 \cdot l \cdot atm \cdot mole^{-1} \cdot K^{-1} \times 298K} = 0.0408 \text{ mole}$$

$$\Delta S = -0.408 \times 1.987 \left(\ln \frac{1}{3} + \ln \frac{2}{3} \right) = 1.219 \text{ cal K}^{-1}$$

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2.3.5. ABSOLUTE VALUE OF ENTROPY

2.3.5.1. The heat capacity of uranium metal is 0.727 cal mole^{-1} K^{-1} at 20 K. Calculate the standard absolute entropy of this substance in cal K^{-1} mole at 20 K.

Solution

$$C_P \approx C_V = aT^3 \; ; \; a = \frac{C_V}{T^3} = \frac{0.727}{(20)^3} = 9.09 \times 10^{-5}$$

$$C_V = 9.09 \times 10^{-5} T^3$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V dT}{T} = \int_0^{20} 9.09 \times 10^{-5} T^2 dT$$

$$= \frac{1}{3} \times 9.09 \times 10^{-5} \left(20^3 - 0^3\right) = 0.242 \text{ cal K}^{-1} \text{ mole}^{-1}$$

2.3.5.2. Estimate the zero-point entropy of NO.

Solution

In the solid state NO is capable of existing in two orientations, which have practically equal chances of existence. These are NO NO and NO ON. The zero-point entropy is therefore

$$S = k \ln 2^N = Nk \ln 2 = R \ln 2 = 1.99 \times 2.30 \times 0.0301 = 1.38 \text{ cal K}^{-1} \text{ mole}^{-1}$$

where k = Boltzmann's constant and N = Avogadro's number

2.3.5.3. Explain the following statements in statistical terms:

(a)The entropy change in a chemical reaction approaches zero as the temperature approaches 0 K.

(b) The reaction $2C(graphite) + O_2(crystal) \rightarrow 2CO(crystal)$ is an exception to this rule.

Solution

(a) $S = k \ln \Omega$ where Ω is the number of detailed (molecular) states corresponding to the given gross (macroscopic) state. Usually, at 0 K, $\Omega = 1$ for each reactant and product, therefore $S = 0$ for each reactant and product and $\Delta S = 0$ at 0 K.

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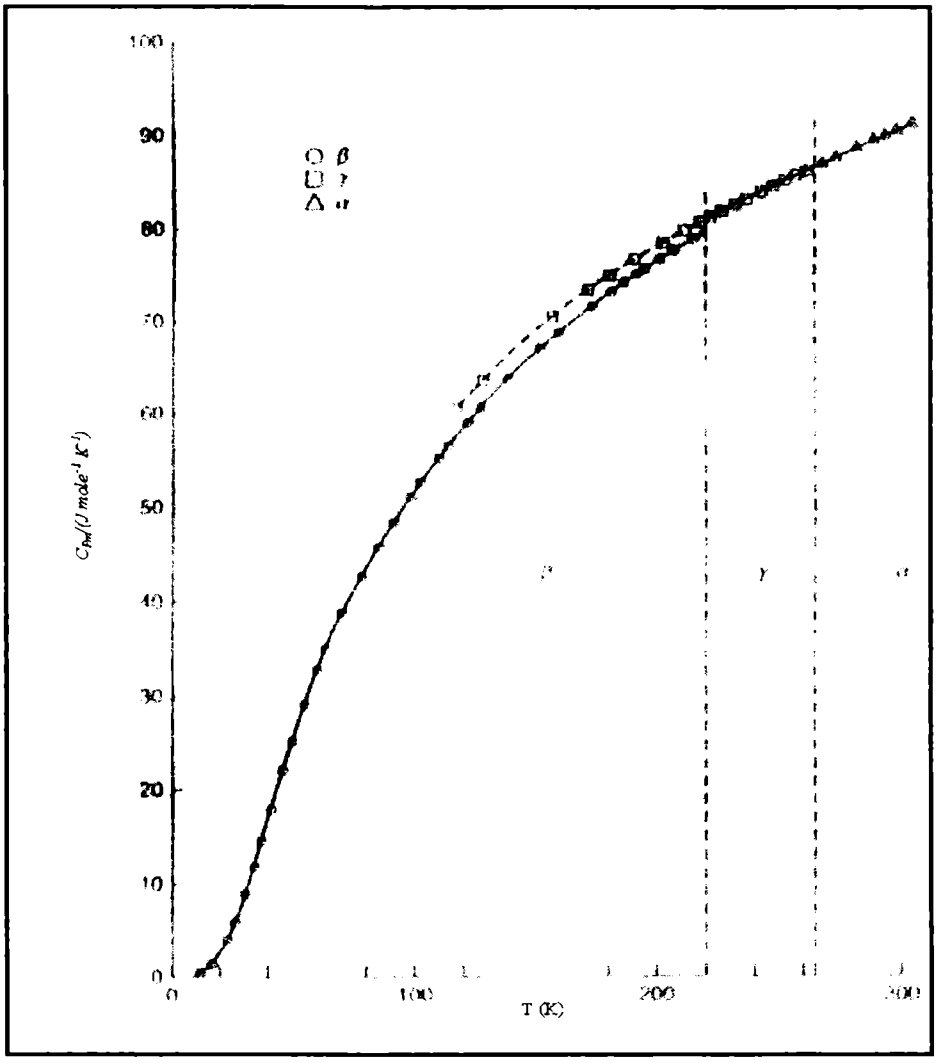
(b) For C and O_2, $\Omega = 1$ and $S = 0$ as usual. For CO, the dipole moment is so small that the orientation of the molecules (CO or OC) in the crystal is nearly random even at 0 K. Thus $\Omega > 1$ and thus $S > 0$ for CO and $\Delta S > 0$ for the reaction.

2.3.5.4. Calculate the absolute value of entropy of methylammonium chloride at 298 K using the values of the heat capacity from chart. Debye equation for the region 0 – 20 K is:

$$C_P = C_V = 1943.8\frac{T^3}{\theta^3} \text{ J mole}^{-1} \text{ K}^{-1}$$

with $\theta = 200.5$ K and expresses the behavior of the heat capacity up to 124 K. between 0 K and 220.4 K the substance is in β solid crystalline modification, between 220.4 K and 264.5 K the substance is in γ modification and between 264.5 K and 298.15 K the substance is in α modification.



Heat capacities of the three allotropic forms, α, β, γ, of methyl ammonium chloride. The dashed curve represents the heat capacity of the metastable γ form, super cooled.

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Solution

We can calculate the entropy by integrating equation

$$S(T) = \int_0^T \frac{C_P dT}{T}$$

for each allotrope in the temperature region in which it is most stable and then adding the entropies of transition.

Step 1. CH_3NH_3Cl (s, β form, 0 K) = CH_3NH_3Cl (s, β form, 12.04 K)

$$\Delta S_1 = \int_{0K}^{12.04K} \frac{C_P dT}{T} = 0.280 \text{ J mole}^{-1}\text{K}^{-1} \text{ (Debye equation with } \theta = 200.5 \text{ K)}$$

Step 2. CH_3NH_3Cl (s, β form, 12.04 K) = CH_3NH_3Cl (s, β form, 220.4 K)

$$\Delta S_2 = \int_{2.04K}^{220.4K} \frac{C_P dT}{T} = 93.412 \text{ J mole}^{-1}\text{K}^{-1} \text{ (numerical integration)}$$

Step 3. CH_3NH_3Cl (s, β form, 220.4 K) = CH_3NH_3Cl (s, γ form, 220.4 K)

$$\Delta S_3 = \frac{\Delta^m H}{T} = \frac{1779.0}{220.4} = 8.072 \text{ J mole}^{-1}\text{K}^{-1}$$

Step 4. CH_3NH_3Cl (s, γ form, 220.4 K) = CH_3NH_3Cl (s, γ form, 264.5 K)

$$\Delta S_4 = \int_{220.4K}^{264.5K} \frac{C_P dT}{T} = 15.439 \text{ J mole}^{-1}\text{K}^{-1} \text{ (numerical integration)}$$

Step 5. CH_3NH_3Cl (s, γ form, 264.5 K) = CH_3NH_3Cl (s, α form, 264.5 K)

$$\Delta S_5 = \frac{\Delta^m H}{T} = \frac{2818.3}{264.5} = 10.655 \text{ J mole}^{-1}\text{K}^{-1}$$

Step 6. CH_3NH_3Cl (s, α form, 264.5 K) = CH_3NH_3Cl (s, α form, 298.15 K)

$$\Delta S_6 = \int_{264.5K}^{298.15K} \frac{C_P dT}{T} = 10.690 \text{ J mole}^{-1}\text{K}^{-1} \text{ (numerical integration)}$$

Addition of Steps 1 – 6 gives

Step 7. CH_3NH_3Cl (s, β form, 0 K) = CH_3NH_3Cl (s, α form, 298.15 K)

and

$$\Delta S^o = \sum_1^6 \Delta S_i = 138.548 \text{ J mole}^{-1}\text{K}^{-1}$$

Thus for methyl ammonium chloride S^o_{298K} is 138.548 J $\text{mole}^{-1}\text{K}^{-1}$.

2.3.5.5. Calculate the absolute value of entropy of cyclopropane, like an ideal gas (P = 0.1 MPa = 1 atm), at the boiling point 240.3 K if Debye equation for region 0-15 K is $C_P = C_V = 662T^3/\theta_3$ J $\text{mole}^{-1}\text{K}^{-1}$ with θ = 130 K, $C_l^S = 28.97$ J $\text{mole}^{-1}\text{K}^{-1}$,

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$\Delta^f H = 5443.3$ J mole^{-1}, $C_P^l = 76.56$ J mole^{-1}K^{-1}, $\Delta^V H = 20.054$ J mole^{-1}K^{-1}.

Solution

Step 1. C_3H_6 (s, 0 K) = C_3H_6 (s, 15 K)

$$\Delta S_1 = 1.016 \text{ J mole}^{-1}\text{K}^{-1} \text{ (Debye equation with } \theta = 130 \text{ K)}$$

Step 2. C_3H_6 (s, 15 K) = C_3H_6 (s, 145.54 K)

$$\Delta S_2 = 65.831 \text{ J mole}^{-1}\text{K}^{-1}$$

Step 3. C_3H_6 (s, 145.54 K) = C_3H_6 (l, 145.54 K)

$$\Delta S_3 = \frac{\Delta^f H}{T} = 37.401 \text{ J mole}^{-1}\text{K}^{-1}$$

Step 4. C_3H_6 (l, 145.54 K) = C_3H_6 (l, 240.30 K)

$$\Delta S_4 = 38.390 \text{ J mole}^{-1}\text{K}^{-1}$$

Step 5. C_3H_6 (l, 240.30 K) = C_3H_6 (real gas, 240.30 K)

$$\Delta S_5 = \frac{\Delta^V H}{T} = 83.454 \text{ J mole}^{-1}\text{K}^{-1}$$

Summing Steps 1 – 5 we obtain

Step 6. C_3H_6 (s, 0 K) = C_3H_6 (real gas, 240.30 K)

$$\Delta S = \sum_1^5 \Delta S_i = 226.09 \text{ J mole}^{-1}\text{K}^{-1}$$

at a pressure of the real gas equal 0.1 MPa (1 atm).

The critical constants used for the correction for gas imperfection are T_c = 375 K and P_c = 5. 65 MPa. Thus for the transformation

Step 7. C_3H_6 (real gas, 240.30 K) = C_3H_6 (ideal gas, 240.30 K)

Equation yields $(S_i - S)_{P=0.1MPa} = \frac{27}{32}\frac{R}{P_c} \cdot \frac{T_c^3}{T^3}(0.1MPa)$

$$\Delta S_7 = 0.53 \text{ J mole}^{-1}\text{K}^{-1}$$

Therefore the entropy $S^o_{240.30K}$ of cyclopropane in the ideal gas (i.e., standard) state is 226.63 J mole^{-1}K^{-1}.

The correction for gas imperfection may seem small. However, we should keep in mind that an error of – 0.4 J mole^{-1}K^{-1} affects the free energy by about 125 J mole^{-1} near room temperature since ΔS would be multipled by T. An error of 125 J mole^{-1} would change an equilibrium constant of 1.00 to 1.05, a difference of 5%.

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2.3.5.6. At 300 K, the compound A is crystalline; the element B and the compound AB_2 are an ideal gases. B is crystalline below 100K and it sublimes (its vapor pressure becomes 1 atm) at this temperature, with the enthalpy of sublimation equal to 2000 cal mole^{-1}. For B (c) below 100K the heat capacity is given by equation

$C_P^0 = 2.5\times10^{-4}T^3 - 2.40\times10^{-10}T^6$ (cal K^{-1} mole^{-1})

Above 100 K, $C_P^0 = 6.00$ cal K^{-1} mole^{-1} for B (g). Enthalpies of formation and third – low entropies for the compounds at 300 K are as follows:

	ΔH_{300}^0 (kcal mole)$^{-1}$	ΔS_{300}^0 (cal K^{-1} mole^{-1})
A (C)	- 10	15
AB_2 (g)	- 41	55

(a) Find the standard third-low entropy of B (g) at 300 K.

(b) An ΔG^0 for the reaction $A(C)+2B(g) \Leftrightarrow AB_2(g)$.

Solution

(a) $S^0 = \int_0^{100} \frac{C_P^o}{T}dT + \frac{2000}{100} + 6\ln\frac{300}{100}$

$$= \frac{1}{3}\times2.50\times10^{-7}100^3 - \frac{1}{6}\times2.40\times10^{-10}\times100^6 + 20.0 + 600\times1.099 = 69.9 \text{ calK}^{-1}\text{mole}^{-1}$$

(b) $A(C)+2B(g) \rightarrow AB_2(g)$

H_{300}	- 10	0	- 41	kcal mole^{-1}
S_{300}	15	2(69.9)	55	cal K^{-1} mole^{-1}

ΔH_{300}^0 = - 31kcal mole^{-1}; ΔS_{300}^0 = -99.8 cal K^{-1} mole^{-1}

$\Delta G_{300}^0 = \Delta H_{300}^0 - 300\Delta S_{300}^0$ = - 1060 cal mole^{-1}

2.3.5.7. By measurement of equilibrium constant for the reaction

H_2O (l) + CO (g) $\Leftrightarrow$ HCOOH (l), was found that the standard free energy formation of formic acid from the elements is –85.200 cal mole^{-1} at 298°K. The standard free energy formation of formic acid from the elements at 298°K is –85.370 cal mole^{-1} by heat capacity measurements. The two results may be considered to be identical within limits experimental error. How does the agreement between the two results offer experimental evidence for the validity of the third law of thermodynamics?

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Solution

The calculation of ΔG_f^0 from the measurements of the equilibrium constant was not based on the assumption of the validity of the third-law, whereas the calculation of ΔG_f^0 from the heat capacities was. The agreement between the two results is therefore evidence that it was valid to apply the third low in the later case.

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2.4. GIBBS AND HELMOLTZ FREE ENERGIES AND CORRELATIONS

2.4.1. The functions F and G are useful as criteria for spontaneity $\Delta F_{T,V} \leq 0$ and $\Delta G_{T,P} \leq 0$ because $dF_{T,V} = \delta Q - TdS$ and $dG_{T,P} = \delta Q - TdS$, they both reduce under the indicated restrictions to $\delta Q - TdS$.

Can we define a new function, X, such that $dx = \delta Q - TdS$ directly with no restrictions on T, P or V?

Solutions

Both δQ and TdS are inexact differentials (though dS is an exact one); the dX thus defined would also be inexact. (It is possible for the sum or difference of two inexact differentials to be an exact differential but this is exceptional: $dE = \delta Q + \delta W$ is an exemple).

In other words we would not have defined a function X determined by the state of the system. The change in X would depend on the path by which the new state was reached from the old state. On the other hand the general definitions of F and G are such that their differentials are exact ones: $F = E - TS$; $dF = dE - TdS - SdT = \delta Q + \delta W - TdS - SdT$.

If V is constant and there is no work other from pressure-volume work, $\delta W = 0$; if T is constant $SdT = 0$. Then $dF_{T,V} = \delta Q - TdS$ and this differnce of inexact differentials is exact when the paths are thus restricted.

Similarly,

$$dG = dF + PdV + VdP = \delta Q + \delta W + PdV + VdP - TdS - SdT$$

$$dG_{T,P} = \delta Q - TdS$$

When T and P are constant and $\delta W = - PdV$.

2.4.2. Ethylene (C_2H_4) can be purchased in cylinders or tank cars or by pipeline. For the reaction

$C_2H_4(g) = 2C$ (graphite) $+ 2H_2(g)$ at 25°C, $\Delta G° = -16$ kcal.

(a) Is the decomposition of C_2H_4 spontaneous?

(b) Does C_2H_4 decompose at room temperature?

(c) Explain any apparent discrepancy between your answers to (a) and (b).

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Solution

(a) $\Delta G < 0$. Therefore the reaction is spontaneous.

(b) No.

(c) "Spontaneous", in Thermodynamics, means "not impossible". There is no thermodynamic reason why C_2H_4 cannot decompose at 25°C. For some extra thermodynamic reason the rate of this reaction is zero (high activation energy).

2.4.3. At 298.15 K and 1.00 atm, ΔG for the conversion of rombic sulfur is 18 cal mole^{-1}. Which of the two phases is stable under these conditions? The density of rhombic sulphur is 1.96 g cm^{-3}; that of monoclinic 2.07 g cm $^{-3}$. Estimate the minimum pressure at which the other phase would be stable at 298.15°K.

Solution

Rhombic sulfur is stable.

$d(\Delta G) = \Delta V\, dP$

$\Delta G_2 - \Delta G_1 = \Delta V\,(P_2 - P_1)$

$$(0 - 18)\ \text{cal mole}^{-1} = \left(\frac{1}{2.07} - \frac{1}{1.96}\right)\text{cm}^3\ \text{g}^{-1} \times 32\ \text{g mole}^{-1} \times (P_2 - 1)\ \text{atm} \times \frac{1cal}{41.3cm^3 atm}$$

$P_2 = 858$ atm.

2.4.4. The process $2H_2$(g, 1 atm, 25°C) + O_2(g, 1 atm, 25°C) $\rightarrow$ $2H_2O$ (l, 1 atm, 25°C) is usually regarded as "spontaneous" (that is , thermodynamically possible). Is it possible to carry out the process under conditions of (a) isolation, (b) constant temperature and pressure, (c) constant temperature and volume? Explain.

Solution

(a) No. The product would be steam at much higher temperature and pressure.

(b) Yes. $\Delta G < 0$ and the process is possible. These are the conditions which one usually has in mind when it says that a process is or is not "spontaneous".

(c) No. If V and T are kept constant, the pressure will fall because of the loss of gas.

2.4.5. At 298.2 K the standard free energy of solution $MgCl_2 \cdot 6H_2O$ is –6,180 cal mole^{-1} and the standard free energies of formation of $MgCl_2 \cdot 6H_2O$, H_2O and Cl^- (aq) are: -505,410 cal·mole^{-1}, -56,693 cal·mole^{-1} and –31,340 cal (g atom)$^{-1}$, respectively. Calculate the standard free energy of formation of the aqueous magnesium ion at this temperature.

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Solution

	ΔG^0
$Mg + Cl_2 + 6H_2 + 3O_2 \rightarrow MgCl_2 \cdot 6H_2O$	-505,410
$6H_2O \rightarrow 6H_2 + 3O_2$	-6(-56.593) =340,158
$2Cl^-(aq) \rightarrow Cl_2 + 2e^-$	-2(-31.340) = 62,680
$MgCl_2 \cdot 6H_2O + aq = Mg^{2+}(aq) + 2Cl^-(aq) + 6H_2O$	-6,180
$Mg \rightarrow Mg^{2+}(aq) + 2e^-$	-108,752 cal (g ion)$^{-1}$

2.4.6. Process A: One mole of an ideal monoatomic gas expands isothermally at 300 K into a vacuum from an initial volume of 10 liters to a final volume of 20 liters.

Process B: One mole of the same gas expands isothermally and reversibly at 300 K from 10 to 20 liters.

(a) For each of the two processes, calculate Q, W, ΔE, ΔH, ΔF and ΔG.

(b) Describe a process by which the gas could be restored to its initial state after each of the processes A and B. Show how the surroundings could also be restored to their initial state after one process, and how the surroundings could not be restored to their initial state after the other process.

Solution

(a) Process A:

$Q_A = W_A = 0$

Process B

$$Q_B = W_B = RT\ln\frac{V_2}{V_1} = 1.987 \text{ x } 300 \ln 2 = 413 \text{ cal.}$$

Either process

$\Delta E = \Delta H = 0$

$\Delta F = \Delta G = -RT\ln 2 = -413$ cal.

(b) The gas can be compressed isothermally and reversibly from 20 l to 10 l.The work done on the gas in this process is 413 cal. In process B this amount of work was done by the gas and stored in the surroundings from which it can now be withdrawn, thus restoring the surroundings as well as the gas to initial state. In process A, however the gas did no work and the 413 cal needed, must be obtained by, for example, letting a weight fall. thus leaving the surroundings in a state different from the initial state.

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If the reverse process is carried out irreversibly, more than 413 cal of work must be done on the gas and the restoration of the surroundings to their initial states is more clearly impossible.

2.4.7. The thermodynamic equation of state,

$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ applies to all substances.

Derive it starting only with the first and second laws of thermodynamics.

Solution

dE = δQ + δW (first law) or dE = δQ – PdV

dS = $\frac{\delta Q_{rev}}{T}$ (second law)

Since the final explanation is to apply only to systems in equilibrium, we can use this relationship

dE = TdS – PdV

$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$

Now F = E– TS (definition of F)

dF = dE – TdS – SdT = TdS – PdV – TdS – SdT = -PdV –SdT

$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$

and $\left(\frac{\partial F}{\partial T}\right)_V = -S$ and $\left(\frac{\partial F}{\partial V}\right)_T = -P$

The mixed second derivatives of the function F:

$\frac{\partial^2 F}{\partial T \partial V} = -\left(\frac{\partial S}{\partial V}\right)_T$ and $\frac{\partial^2 F}{\partial V \partial T} = -\left(\frac{\partial P}{\partial T}\right)_V$

hence $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ and $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

2.4.8. Derive the formula $\left(\partial H/\partial P\right)_T = V - T\left(\partial V/\partial T\right)_P$ using the first and second law of thermodynamics.

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Solution

$H = E + PV$

$dH = dE + PdV + VdP = \delta Q + VdP = TdS + VdP$

$$\left(\frac{\partial H}{\partial P}\right)_T = V + T\left(\frac{\partial S}{\partial P}\right)_T$$

On the other hand

$G = H - TS$

$dG = dH - TdS - SdT = d(E+PV) - SdT - TdS$

$= dE + PdV + VdP - SdT - TdS =$

$= \delta Q + VdP - SdT - TdS$

$= VdP - SdT$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

hence

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V$$

The mixed second derivatives are:

$$\frac{\partial^2 G}{\partial T \partial P} = -\left(\frac{\partial S}{\partial P}\right)_T \text{ and } \frac{\partial^2 G}{\partial P \partial T} = \left(\frac{\partial V}{\partial T}\right)_P$$

The final result is:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

2.4.9. For the reaction:

$2H_2S(g) + 3O_2(g) = 2SO_2(g) + 2H_2O(l)$

ΔH^0_{298} = - 1130.5 kJ, ΔS^0_{298} = - 3.88.3 j K^{-1}, and ΔC^0_P = 74.0 j K^{-1}. Express ΔH^0, ΔE^0, ΔG^0, and ΔS^0 for this reaction as function of temperature, containing only T and actual numbers. Make, and point out, any reasonable and necessary approximations.

Solution

$$\Delta H^0_T = \Delta H^0_{298} + \int_{298}^{T} \Delta C^0_P dT = -1130.5 + 0.0740(T - 298) = \text{ -1152.6 +0.074 T (kj)}$$

It has been assumed that ΔC^0_P is independent of T.

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$\Delta E_T^0 = \Delta H_T^0 - \Delta\nu RT = -1152.6 + 0.0989\ T$ (kj)

It has been assumed that the gas are ideal and that PV for H_2O (l) is negligible.

$$\Delta S_T^0 = \Delta S_{298}^0 + \int_{298}^{T} \frac{\Delta C_P^0}{T} dT = -383.3 + 74 \ln\left(\frac{T}{298}\right) = -810 + 74 \ln T\ (jK^{-1})$$

$\Delta G_T^0 = \Delta H_T^0 - T\Delta S_T^0 = -1152.6 + 0.884T - 0.074 \ln T$ (kj)

2.4.10. (a) Find ΔH^0 at 1000°K for the reaction

$$NaCl(s) \rightarrow Na(g) + \frac{1}{2} Cl_2(g)$$

For this reaction

$\Delta H_{298}^0 = 124.1$ kcal

and

$\Delta C_P^0 = -1.585 - 3.82 \times 10^{-3} T - 0.34 \times 10^5\ T^{-2}$

(b) It is true that $\Delta S^0 = \Delta H°/T$ for (i) the reaction in (a) at 25)C; (ii) the process NaCl(s) = NaCl(g) at 25°C; (iii) the process NaCl(l)= NaCl(g) at 1413°C, the boiling point of NaCl? Explain in each case. Assume that gases are ideal.

Solution

$$\Delta H_{1000}^0 = \Delta H_{298}^0 + \int_{298}^{1000} \Delta C_P^0 dT = \Delta H_{298}^0 + \int_{298}^{1000} (-1.585 - 3.82 \cdot 10^{-3} T - 0.34 \cdot 10^{-5} T^{-2}) dT$$

$$= 124.100 - 1.585(1000 - 298) - \frac{3.82}{2} \times 10^{-3} (1000^{+2} - 298^{+2}) - \frac{0.34 \times 10^{-5} (1000 - 298)}{1000 \times 298}$$

$= 121.1$ kcal

(a) For any isothermal process

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T}$$

and $\Delta S^0 = \Delta H^0 / T$ only when $\Delta G^0 = 0$.

(i) No; we know by experience that $\Delta G^0 >> 0$ for this highly nonspontaneous process.

(ii) No; for this process, also, $\Delta G^0 >> 0$. The superscript implies that the fugacity of NaCl (g) is 1 atm and we know that the fugacity of saturated NaCl vapor is

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much less than 1 atm at 25°C.

(iii) Yes; the fugacity (and the vapor pressure, since we assume ideality) of NaCl at its boiling point is 1 atm and when the process is carried out reversibly and isothermally at this constant pressure, the work done, excluding pressure work, is 0. Thus $\Delta G^0 = 0$.

2.4.11. Evaluate ΔG and ΔH for the isothermal reversible expansion of 1 mole of a gas with the equation of state PV= RT(1 + B/V) from volume V_1 to volume V_2 at temperature T.

Solution

PV=RT+RTB/V

dG = VdP – SdT; $dG_T = VdP$

$PdV + VdP = -\frac{RTB}{V^2}dV$; $VdP = -PdV - \frac{RTB}{V^2}dV$, and because $P = \frac{RT}{V} + \frac{RTB}{V^2}$

$$VdP = -\left(\frac{RT}{V} + \frac{2RTB}{V^2}\right)dV$$

$$\Delta G_T = -\int_{V_1}^{V_2} RT\frac{dV}{V} - \int_{V_1}^{V_2} 2RTB\frac{dV}{V^2} = \text{- RT ln}\left(\frac{V_2}{V_1}\right) + 2\text{RTB}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$\left(\frac{\partial F}{\partial V}\right)_T = -P$$

$$\Delta F_T = -\int_{V_1}^{V_2} PdV = -RT\int_{V_1}^{V_2}\left(\frac{1}{V} + \frac{B}{V^2}\right)dV = -RT\left[\ln\frac{V_2}{V_1} - B\left(\frac{1}{V_2} - \frac{1}{V_1}\right)\right]$$

We can also evaluate ΔG by

$$\Delta G = \Delta F + \Delta(PV) = \text{- RT ln}\left(\frac{V_2}{V_1}\right) + \text{RTB}\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + \text{RTB}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$= \text{- RT ln}\left(\frac{V_2}{V_1}\right) + 2\text{RTB}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

2.4.12. For N_2O at 0°C the fugacity coefficient γ = f/P is 0.9847 at 3 atm and 0.6961 at 60 atm. Evaluate ΔG in calories for the isothermal, reversible compression of 1 mole of this substance from 3 to 60 atm at 0°C, (a) assuming ideal gas behaviour, (b) using the

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fugacity data given above.

Solution

$$\Delta G = \int_{P_1}^{P_2} V dP = RT \ln \frac{P_2}{P_1} = 1.987 \text{ x } 273.2 \text{ x } 2.303 \lg \frac{60}{3} = 1628 \text{ cal}$$

$$\Delta G = RT \ln \frac{f_2}{f_1} = 1.987 \text{ x } 2.303 \text{ x } 273.2 \lg \left(\frac{60 \times 0.6961}{3 \times 0.9847} \right) = 1440 \text{ cal}$$

2.4.13. Evaluate ΔG for the isothermal, reversible compression from P_1 to P_2 of 1 mole of a gas that has the equation of state

$$PV = RT \left\{ 1 + \frac{9}{128} \left(\frac{P}{P_c} \right) \left(\frac{T_c}{T} \right) \left[1 - 6 \left(\frac{T_c}{T} \right)^2 \right] \right\}$$

where P_c and T_c are the critical constants.

Solution

$$\Delta G = \int_{P_1}^{P_2} V dP = \int_{P_1}^{P_2} \frac{RT dP}{P} + \int_{P_1}^{P_2} \frac{9R}{128} \frac{T_c}{P_c} \left[1 - 6 \left(\frac{T_c}{T} \right)^2 \right] dP$$

$$= RT \ln \frac{P_2}{P_1} + \frac{9R}{128} \left(\frac{T_c}{P_c} \right) \left[1 - 6 \left(\frac{T_c}{T} \right)^2 \right] (P_2 - P_1) = \frac{P_2}{P_1} + \frac{9R}{128} \frac{T_c}{P_c} \left[1 - 6 \left(\frac{T_c}{T} \right)^2 \right] (P_2 - P_1)$$

2.4.14. A mixture of two gases, X and Y, have the equation of state

$$\frac{PV}{RT} = (n_X + n_Y)(1 + \beta P) + \alpha (n_X n_Y)^{1/2} P$$

Find ΔG_x.

Solution

$$\Delta G_x = \int_{P_1}^{P_2} V_x dP = RT \left[\ln \frac{P_2}{P_1} + (\beta + \frac{1}{2} \times \left(\frac{n_y}{n_x} \right)^{1/2})(P_2 - P_1) \right]$$

2.4.15. Derive the formula

$$\left[\frac{\partial}{\partial T} \left(-\frac{\Delta F}{T} \right) \right]_{P} = -\frac{\Delta E}{T^2}$$

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Solution

$F = E - TS$; $\Delta F = \Delta E + T\left(\frac{\partial \Delta F}{\partial T}\right)_V$ because $dF = -SdT - PdV$

$\left(\frac{\partial F}{\partial T}\right)_V = -S$ and $\left(\frac{\partial \Delta F}{\partial T}\right)_V = -\Delta S$

$$\left[\frac{\partial}{\partial T}\left(\frac{\Delta F}{T}\right)\right]_V = \frac{T\left(\frac{\partial \Delta F}{\partial T}\right) - \Delta F}{T^2} = -\frac{\Delta F - T\left(\frac{\partial \Delta F}{\partial T}\right)_V}{T^2} = -\frac{\Delta E}{T^2}$$

2.4.16. For a certain process

$\Delta G^0_{298} = B$ cal mole^{-1}

$\Delta H° = D + aT + bT^2 + cT^3$

Derive an expression for $\Delta G°$ for this process as a function of temperature.

Solution

$$\left[\frac{\partial\left(\Delta G^0/T\right)}{\partial T}\right]_P = -\frac{\Delta H^0}{T^2} = -\frac{D}{T^2} - \frac{a}{T} - b - cT$$

$$\int_{\left(\Delta G^0/T_1\right)}^{\left(\Delta G^0/T_2\right)} d\left(\Delta G^0/T\right) = -\int_{298}^{T}\frac{DdT}{T^2} - \int_{298}^{T}\frac{adT}{T} - \int_{298}^{T} bdT - \int_{298}^{T} cTdT$$

$$\frac{\Delta G}{T} = \frac{\Delta G_{298}}{298} + D\left(\frac{1}{T} - \frac{1}{298}\right) - a\ln\left(\frac{T}{298}\right) - b(T - 298) - \frac{c}{2}\left(T^2 - 298^2\right)$$

$$\Delta G° = T\left[\frac{B}{298} - \frac{D}{298} + 2.303a\lg 298 + 298b + \frac{c}{2}(298)^2\right] + D - 2.303aT\lg T - bT^2 - \frac{cT^3}{2}$$

2.4.17. Derive a general mathematical expression for $\Delta G°$ as a function of temperature at constant pressure for the reaction $Y_2(g) \leftrightarrows 2Y(g)$. Evaluate all constants. The expression should contain $\Delta G°$ and T as the only variables.

	H^0_{300} (kcal mole^{-1})	S^0_{300} (cal K^{-1} mole^{-1})	C_P (cal K^{-1} mole^{-1})
Y(g)	-150.000	10.00	3.00+2.00 x 10^{-2}T
Y_2(g)	-250.000	30.00	4.00+5.00 x 10^{-2}T

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Solution

ΔH^0_{300} = 2 (-150.000) - 1(-250.000)= - 50,000 kcal

S^0_{300} = 2(10.00) – 1(30.00) = - 10.00 cal K^{-1}

$\Delta G^0_{300} = \Delta H^0_{300}$ - 300 ΔS^0_{300} = - 50.000 – 300(10.00) = - 47.000 kcal

ΔC_P = 2(3.00+2.00 x 10^{-2} T) – (4.00 + 5.00 x 10^{-2} T) = 2.00 - 1.00 x 10^{-2} T

$$\Delta H_T = -50.000 + \int_{300}^{T}\left(2-1\times10^{-2}T\right)dT = -50.000 + 2(T-300) - \frac{10^{-2}}{2}\left(T^2-300^2\right)$$

$$= -50.000 + 2T - 600 - 5\cdot10^{-3}T^2 + 450 = -50.150 + 2T - 5\cdot10^{-3}T^2 \text{ (cal)}$$

$$-\frac{\Delta G_2}{T_2} + \frac{\Delta G_1}{T_1} = \int_{T_1}^{T_2}\frac{\Delta H}{T^2}dT = -\int_{T_1}^{T_2}\frac{50.150}{T^2}dT + \int_{T_1}^{T_2}\frac{2T}{T^2}dT - \int_{T_1}^{T_2}5\times10^{-3}dT$$

$$-\frac{\Delta G_2}{T_2} - \frac{47.000}{300} = -50.150\left(\frac{1}{T_2}-\frac{1}{300}\right) + 2\ln\frac{T_2}{300} - 5\cdot10^{-3}\left(T_2-300\right)$$

$$-\frac{\Delta G_2}{T_2} = -20.409 + \frac{50.150}{T_2} + 4.61\lg T_2 - 5\cdot10^{-3}T_2$$

If $\Delta G_2 = \Delta G$ and $T_2 = T$

ΔG = -50.150 + 20.409 T – 4.61 T lg T + $5\cdot10^{-3}$ T^2 (cal)

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2.5. CHEMICAL POTENTIAL

2.5.1. A person has the following understanding difficulties:

(a) The free energy change for a system, at equilibrium, is supposed to be equal to zero. The equilibrium free energy for the reaction $N_2 + 3H_2O \Leftrightarrow 2NH_3$ is not equal to zero but –7.88 kcal at 298K. If the system is at equilibrium why isn't the free energy equal to zero?

(b) Ice and salt are in equilibrium, at say, -3^{0}C. The activity of the ice is 1.00. The activity of the water in the solution is less than 1.00. In order for the solid and liquid water to be in equilibrium, is it not necessary that their activities be equal?

In each case explain what incorrect assumption have been made, what the corresponding correct statements are, and under what special circumstances, if any, the original assumption and conclusions would become correct.

Solution

(a) The person does not understand the distinction between ΔG and ΔG^0. The criterion for equilibrium is that $\Delta G = 0$, not $\Delta G^0 = 0$. $\Delta G^0 = 0$ only if equilibrium constant equals 1.

(b) A necessary condition for equilibrium between the two phases (l and s) is that $\mu_{1,l} = \mu_{1,s}$, where 1 refers to water. This condition may be written

$$\mu^o_{1,l} + RT \ln a_{1,l} = \mu^o_{1,s} + RT \ln a_{1,s}$$

If $\mu^o_{1,l} = \mu^o_{1,s}$, then, of course, $a_{1,l} = a_{1,s}$ at equilibrium. But in the present case $\mu^o_{1,l}$ is the chemical potential of water, while chemical $\mu^0_{1,s}$ is potential of pure ice, both under 1 atm at –3^{0}C. These are not equal; rather, $\mu^o_{1,s} < \mu^o_{1,l}$ for ice in the stable form. Then it is obvious from above equation that $a_{1,s} > a_{1,l}$, we already know. A case where μ^o is the same in the two phases appears in connection with osmotic pressure; that it is true that the activity of the solvent is the same in the two phases at equilibrium.

2.5.2. G.N. Lewis proposed the term "escaping tendency" to give a strong kinetic-molecular flavor to the concept of partial molar free energy or chemical potential. Let us consider two solution of iodine (I_2) in water (H_2O) and in carbon tetrachloride (CCl_4) which have

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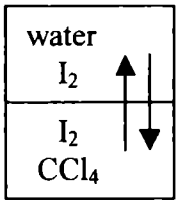
reached equilibrium with each other at a fixed T and P. Explain why the "escaping tendency" of I_2 is greater in H_2O than in CCl_4?

Solution



In the system at equilibrium let us carry out a transfer of an infinitesimal quantity of I_2 from the H_2O to CCl_4 phase. We can write:

$$\mu_{I_{2(H_2O)}} dn_{I_{2(H_2O)}} + \mu_{I_{2(CCl_4)}} dn_{I_{2(CCl_4)}} = 0$$

In this closed system any loss of I_2 from the H_2O phase is accompanied by an equivalent gain in the CCl_4, thus

$$-dn_{I_{2(H_2O)}} = dn_{I_{2(CCl_4)}}$$

Hence

$$\mu_{I_{2(H_2O)}} dn_{I_{2(H_2O)}} + \mu_{I_{2(CCl_4)}} [-dn_{I_{2(H_2O)}}] = 0$$

It follows that

$$\mu_{I_{2(H_2O)}} = \mu_{I_{2(CCl_4)}}$$

for this system in equilibrium at constant T and P.

Now, we consider that I_2 will diffuse spontaneously, at constant T and P, from H_2O into CCl_4. In this case the concentration in water and water phase in greater than that which would exit in equilibrium with CCl_4 phase so we can write

$$\mu_{I_{2(H_2O)}} dn_{I_{2(H_2O)}} + \mu_{I_{2(CCl_4)}} dn_{I_{2(CCl_4)}} < 0$$

For the spontaneous diffusion of iodine, equation $-dn_{I_{2(H_2O)}} = dn_{I_{2(CCl_4)}}$ is valid in this closed system. Hence

$$\mu_{I_{2(H_2O)}} dn_{I_{2(H_2O)}} + \mu_{I_{2(CCl_4)}} [-dn_{I_{2(H_2O)}}] < 0 \text{ or } [\mu_{I_{2(H_2O)}} - \mu_{I_{2(CCl_4)}}] dn_{I_{2(H_2O)}} < 0$$

Since the H_2O loses I_2: $dn_{I_{2(H_2O)}} < 0$

That is *dn* is a negative number. In this case the last inequation is valid only if the difference in chemical potential is a positive number.

That means:

$$\mu_{I_{2(H_2O)}} > \mu_{I_{2(CCl_4)}}$$

And we can say that the "escaping tendency" of the I_2 is greater in the H_2O than in CCl_4 phase.

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2.5.3. Calculate the chemical potential variation of one mole of ideal gas component in a mixture in an isothermal expansion from 1 *l* to 10 *ls* at 298 K.

Solution

$$\left(\frac{\partial \mu}{\partial P}\right)_{T,n_g} = \overline{V}_i = \frac{RT}{P}$$

$$d\mu_i = \frac{RT}{P} dP = RTd\ln P$$

Because $P = \frac{RT}{V}$; $dP = -\frac{RT}{V^2} dT$ and $\frac{dP}{P} = -\frac{\frac{RT}{V^2} dV}{\frac{RT}{V}} = -\frac{dV}{V}$

Hence

$$d\mu = -RTd\ln V$$

and $\Delta\mu = -RT \int_{V_1}^{V_2} d\ln V = -1.987 \times 298 \times \ln 10$

$$= -4.565 \times 298 \times \lg 10 = -1{,}360.37 \text{ cal mole}^{-1}$$

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2.6. CHEMICAL EQUILIBRIUM

2.6.1. STANDARD GIBBS ENERGY AND EQUILIBRIUM CONSTANT

2.6.1.1. The standard free energy of formation of CO_2 (g) is – 94.260 kcalmole^{-1}. Calculate the equilibrium constant for reaction

C (graphite) + O_2 (g) ⇆ CO_2 (g)

Solution

$$\Delta G_r^o = \Delta G_{f_{CO_2}}^o - \Delta G_{f_{C(gr)}}^o - \Delta G_{f_{O_2}}^o = -94.260$$

$$\Delta G_r^o = -RT \ln K$$

Hence

$$K = e^{-\frac{\Delta G_r^o}{RT}} = e^{-\frac{-94.260}{1.987 \times 298.16}} = 1.252$$

2.6.1.2. Using data from the table below calculate the value of equilibrium constant for the reaction 3 HC ≡ CH (g) ⇆ C_6H_6 (g)

acetylene benzene

at 25^{0}C assuming ideal gas behavior. Would you recommend this process as a practical method for making benzene? Explain.

	ΔG_f^o, (cal mole^{-1})
HC ≡ CH	50,000
C_6H_6	29,760

Solution

$$\Delta G^o = 29{,}760 - 3(50{,}000) = -120{,}240 \text{ cal}$$

$$\log K = \frac{-\Delta G^o}{2.303RT} = \frac{-(-120{,}240)}{2.303 \times 1.987 \times 298.2} = 88.2$$

$$K = 2 \times 10^{88}$$

Since the equilibrium constant is so large this might be a practical method.

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2.6.1.3. For the reaction

$CO\ (g) + SO_3\ (g) \leftrightarrows CO_2\ (g) + SO_2\ (g)$,

$\Delta H^o_{298} = -44.14$ kcal and $\Delta G^o_{298} = -44.72$ kcal.

Calculate (a) ΔG^o_{398}; (b) $K_{P,\,398}$. Assume that $\Delta C^o_P = 0$ between 298 and 398^0K.

Solution

(a) $$\frac{\Delta G^o_{398}}{398} = \frac{\Delta G^0_{298}}{298} - \int_{298}^{398} \frac{\Delta H^o}{T^2} dT = \frac{-44.72}{298} + 44.14\left(\frac{1}{398} - \frac{1}{298}\right)$$

$$= -0.15006 - 0.0372 = -0.187$$

$\Delta G^o_{398} = -74.426$ kcal

(b) $$\ln K_P = -\frac{\Delta G^o}{RT}$$

$$\lg K_P = \frac{0.187}{2.303 \times 1.987 \times 10^{-3}} = 40.86$$

$$K_P = 7.325 \cdot 10^{40}$$

2.6.1.4. In the table are the following data:

(cal K^{-1} $mole^{-1}$) at 27°C	S^o	C^o_P
O_2 (g)	49.0	7.0
S (s)	7.6	4.4
Te (s)	11.9	6.0
H_2O (l)	16.7	18.0
H_2S (g)	48.6	8.3
SO_2 (g)	69.2	8.6
TeO_2 (s)	17.2	13.5

ΔH^o for reactions at 27°C in kcal $mole^{-1}$ are:

$S\ (s) + O_2\ (g) \rightarrow SO_2\ (g)$	- 70.96
$Te\ (s) + O_2\ (g) \rightarrow TeO_2\ (s)$	- 77.69
$2\ H_2S\ (g) + 3\ O_2\ (g) \rightarrow 2\ H_2O\ (l) + 2\ SO_2\ (g)$	- 268.92

Assuming that the gases are ideal, calculate with the aid of above data:

(a) ΔH^o at 27°C for the reaction

$2\ H_2S\ (g) + TeO_2\ (s) \leftrightarrows Te\ (s) + 2\ S\ (s) + 2\ H_2O\ (l)$

(b) ΔH^o at 77°C for the same reaction.

(c) ΔG^o at 77°C for the same reaction.

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(d) The pressure of H_2S that can exist in equilibrium with a mixture of liquid water and the solids S, Te, and TeO_2 at 77°C.

Solution

(a)

	ΔH^o_{300}
$2\ SO_2\ (g) = 2\ S\ (s) + 2\ O_2\ (g)$	+141.92
$TeO_2\ (s) = Te\ (s) + O_2\ (g)$	+77.69
$2\ H_2S\ (g) + 3\ O_2\ (g) \rightarrow 2\ H_2O\ (l) + 2\ SO_2\ (g)$	-268.92
$2\ H_2S\ (g) + TeO_2\ (s) \leftrightarrows Te\ (s) + 2\ S\ (s) + 2\ H_2O\ (l)$	-19.31 kcal

(b) $\Delta C_P^o = 6.0 + 2\times 4.4 + 2\times 18.0 - 2\times 8.3 - 13.5 = 20.7\ \text{cal K}^{-1}$

$$\Delta H^o_{350} = \Delta H^o_{300} + \int_{300}^{350} \Delta C_P^o dT = -49.31 + 20.7\times 10^{-3}\times 50 = -48.27\ \text{kcal}$$

(c) $\Delta S^o_{300} = 11.9 + 2\times 7.6 + 2\times 16.7 - 2\times 48.6 - 17.2 = -53.9\ \text{cal K}^{-1}$

$$\Delta S^o_{350} = \Delta S^0_{300} + \int_{300}^{350} \frac{\Delta C_P^o}{T} dT = -53.9 + 20.7 \ln \frac{350}{300} = -50.7\ \text{cal K}^{-1}$$

$$\Delta G^o_{350} = \Delta H^o_{350} - T\Delta S^o_{350} = -48.27 - 350(-50.7\times 10^{-3}) = -30.52\ \text{kcal}$$

(d) $$\lg K_P = -\frac{\Delta G^o}{2.303RT} = \frac{30.52}{2.303\times 1.987\times 10^{-3}\times 350} = 19.25$$

$$K_P = 1.14\cdot 10^{19}$$

$$K_P = \frac{1}{P^2_{H_2S}};\quad P^2_{H_2S} = \frac{1}{K_P}$$

$$P_{H_2S} = \sqrt{\frac{1}{K_P}} = \sqrt{\frac{1}{1.14\cdot 10^{19}}} = \sqrt{\frac{9.36}{10^{20}}} = 3.059\times 10^{-10}$$

2.6.1.5. The deamination of aspartic acid

$$^-OOC - \underset{\displaystyle NH_3^+}{\underset{|}{CH_2}} - COO^- \leftrightarrows {}^-OOC - CH = CH - COO^- + NH_4^+$$

is a reversible reaction catalyzed by the enzyme aspartase. For D, α – aspartic acid the equilibrium constant can be expressed by the equation, in the range of temperature of 20 - 60°C.

$$\lg K_{D,\alpha} = 8.188 - \frac{2315.5}{T} - 0.01025T$$

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(a) What is the value of ΔG^o at 25°C

(b) Derive an equation for ΔG^o as a function of the temperature

(c) Calculate the value of ΔH^o at 25°C.

(d) What is the value of ΔS^o at 25°C?

Solution

(a) $\Delta G^o = -RT \ln K = -4.576 \cdot T \lg K = -4.576T\left(8.188 - \frac{2315.5}{T} - 0.01025T\right)$

$= 10.596 - 37.47T + 0.0469T^2$

$\Delta G^o_{298} = 3{,}593 \text{ kcal}$

(b) From Gibbs-Helmholtz equation $\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2}$

$$\Delta H = -T^2\left[\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right)\right] = -T^2\left[\frac{\partial}{\partial T}\left(-37.47 + \frac{10.595}{T} + 0.04695\right)\right]$$

$$= -T^2\left[-\frac{10.595}{T^2} + 0.0469\right] = 10.595 - 0.0469T^2$$

(a) $\Delta H^o_{298} = 10.595 - 0.0469(298)^2 = 6{,}430 \text{ kcal}$

(b) $\Delta G^o_{298} = \Delta H^o_{298} - T\Delta S^o_{298}$; $\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T}$

$$\Delta S^o_{298} = \frac{6{,}430 - 3{,}593}{298} = 9.5 \text{ cal}$$

2.6.1.6. The ionization constant of the bisulfate ion by an indicator method could be described by the equation

$$\lg K = 61.378 - \frac{1857.1}{T} - 23.093 \lg T$$

between 5 and 55°C.

(a) What does the form of the temperature dependence imply about the temperature dependence of ΔC_P?

(b) Calculate ΔG^o, ΔH^o, ΔS^o at 50°C.

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Solution

(a) $\Delta G^o = -RT\ln K = -4.576T\lg K = -4.576T\left(61.378 - \frac{1857.1}{T} - 23.093\lg T\right)$

$= 8498 - 280.86T + 105T\lg T$

$$\frac{\partial}{\partial T}\left(\frac{\Delta G^o}{T}\right) = -\frac{\Delta H^o}{T^2};\quad \Delta H^o = -T^2\left[\frac{\partial}{\partial T}\left(\frac{\Delta G^o}{T}\right)\right]$$

$$\Delta H^o = -T^2\left[\frac{\partial}{\partial T}\left(-280.86 + \frac{8498}{T} + 105\lg T\right)\right] = -T^2\left(-\frac{8498}{T^2} + \frac{105}{T}\right) = 8498 - 105T$$

$$\Delta C_P^o = \left(\frac{\partial \Delta H^o}{\partial T}\right)_P = -105$$

That means ΔC_P^o doesn't depend on temperature

(b) $\Delta G_{323}^o = 2{,}88$ kcal; $\Delta H_{323}^o = -25{,}417$ kcal

2.6.1.7. The equilibrium constant for reaction

(I) $CH_3OH\ (g) + CO\ (g) \leftrightarrows HCOOCH_3\ (g)$

is $K_{P_I} = 2.82 \cdot 10^{-4}$ at 600 K

The equilibrium constant for reaction

(II) $H_2\ (g) + \frac{1}{2}\ HCOOCH_3\ (g) = CH_3OH\ (g)$

$K_{P_{II}} = 0.813$ at the same temperature

Find out the equilibrium constant for the reaction of synthesis of methanol.

Solution

(III) $2\ H_2\ (g) + CO\ (g) = CH_3OH\ (g)$

$$K_{P_I} = \frac{P_{HCOOCH_3}}{P_{CH_3OH} \cdot P_{CO}};\quad K_{P_{II}} = \frac{P_{CH_3OH}}{P_{H_2} \cdot P_{HCOOCH_3}^{1/2}},\ \text{while}\ K_{P_{III}} = \frac{P_{CH_3OH}}{P_{H_2}^2 \cdot P_{CO}}$$

We can find this constant by combining the constants K_{P_I} and $K_{P_{II}}$, namely,

$$K_{P_{III}} = K_I \cdot K_{II}^2 = 2.82 \cdot 10^{-4} \cdot 0.813^2 = 1.86 \cdot 10^{-4}$$

2.6.1.8. The sodium vapor at 10 atm and 1432.5 K has the equilibrium compositions: 71.3 weight percent sodium monomer Na (g) and 28.7 weight percent dimmer Na_2 (g). Calculate K_P for reaction 2 Na (g) $\leftrightarrows$ Na_2 (g) under these conditions.

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Solution

$$\text{Moles Na (g)} = \frac{71.3}{22.990} = 3.101$$

$$\text{Moles } Na_2 \text{ (g)} = \frac{28.7}{45.980} = 0.624$$

Total number of moles = 3.101 + 0.624 =3.725

Mole fractions: $\chi_{Na} = \frac{3.101}{3.725} = 0.832$

$$\chi_{Na_2} = \frac{0.624}{3.725} = 0.167$$

$$K_p = \frac{P_{Na_2}}{P_{Na}^2} = \frac{0.832 \times 10}{(0.167 \times 10)^2} = 2.98 \text{ atm}^{-1}$$

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2.6.2. TEMPERATURE. PRESSURE AND CONCENTRATION. DEPENDENCE OF CHEMICAL EQUILIBRIUM

2.6.2.1. If $\Delta G^o = -RT\ln K$, derive an equation $\ln K = -\frac{\Delta H^o}{RT} + C$, where C is an integration constant.

Solution

$$\frac{\partial}{\partial T}\left(\frac{\Delta G^o}{T}\right) = -\frac{\Delta H^o}{T^2},\quad d\left(\frac{\Delta G^o}{T}\right) = -\frac{\Delta H^o}{T^2}dT$$

$$d\left(-\frac{RT\ln K}{T}\right) = -\frac{\Delta H^o}{T^2}dT$$

$$-Rd\ln K = -\frac{\Delta H^o}{T^2}dT$$

$d\ln K = \frac{\Delta H^o}{RT^2}dT$ and by integration

$$\ln K = -\frac{\Delta H^o}{RT} + C$$

2.6.2.2. For the reaction

$3\ Fe_2O_3\ (s) \leftrightarrows 2\ Fe_3O_4\ (s) + ½\ O_2\ (g)$

$\Delta H^o_{298} = 55.5$ kcal and $\Delta G^o_{298} = 46.5$ kcal

(a) Calculate the equilibrium constant K_P at 25^0C for this reaction.

(b) Calculate the equilibrium constant for this reaction at 125^0C.

(c) Point out any approximations that you make in the calculation of (b).

Solution

(a) $\Delta G^o_{298} = 46.5$ kcal, $\lg K_P = \frac{-\Delta G^o}{2.303RT} = \frac{-46.5}{2.303\times 1.987\times 298.15\cdot 10^{-3}} = -34.1$

$K_P = 7.94\cdot 10^{-35}$

(b) $\Delta H^o_{298} = 55.5$ kcal, $\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H^o}{RT^2}dT$

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$$\lg K_{T_2} = \lg K_{T_1} + \frac{1}{2.303RT}\int_{T_1}^{T_2}\frac{\Delta H^o}{T^2}dT = \lg K_{T_1} + \frac{\Delta H^o(T_2 - T_1)}{2.303RT_1T_2}$$

$$= -34.1 + \frac{55.5 \times 100}{2.303 \times 1.987 \times 10^{-3} \times 298.15 \times 398.15} = -23.9$$

$$K_{398} = 1.3 \times 10^{-24}$$

(c) The assumption was made that ΔH^o is temperature independent in the range 25 – 125^{0}C.

2.6.2.3. K_P is 1.46 al 100.0^{0}C and 0.54 at 140.0^{0}C for the reaction

$2\ B_5H_{11}\ (g) + 2\ H_2\ (g) \leftrightarrows 2\ B_4H_{10}\ (g) + B_2H_6\ (g)$.

Estimate ΔH^o for this reaction in kilocalories.

Solution

$$\lg\left(\frac{K_{P_2}}{K_{P_1}}\right) = -\frac{\Delta H^o}{2.303}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\lg\left(\frac{0.54}{1.46}\right) = -\frac{\Delta H^o}{2.303}\left(\frac{1}{413.2} - \frac{1}{373.2}\right)$$

$\Delta H^o = -7630$ cal = - 7.63 kcal

2.6.2.4. The following data for the reactions are listed in table.

$FeO\ (s) + CO\ (g) \leftrightarrows Fe\ (s) + CO_2\ (g)$ $\qquad K_1 = \frac{P_{CO_2}}{P_{CO}}$

$Fe_3O_4\ (s) + CO\ (g) \leftrightarrows 3\ FeO\ (s) + CO_2\ (g)$ $\qquad K_2 = \frac{P_{CO_2}}{P_{CO}}$

$t(^oC)$	K_1	$\lg K_1$	K_2	$\lg K_2$	$1/T(10^4)(K^{-1})$
600	0.871	- 0.06	1.15	0.06	11.45
700	0.678	- 0.17	1.77	0.25	10.28
800	0.552	- 0.26	2.54	0.41	9.32
900	0.466	- 0.33	3.43	0.53	8.52
1000	0.403	- 0.39	4.42	0.645	7.85

Calculate the temperature at which Fe, FeO. Fe_3O_4, CO and CO_2 could all exist in equilibrium.

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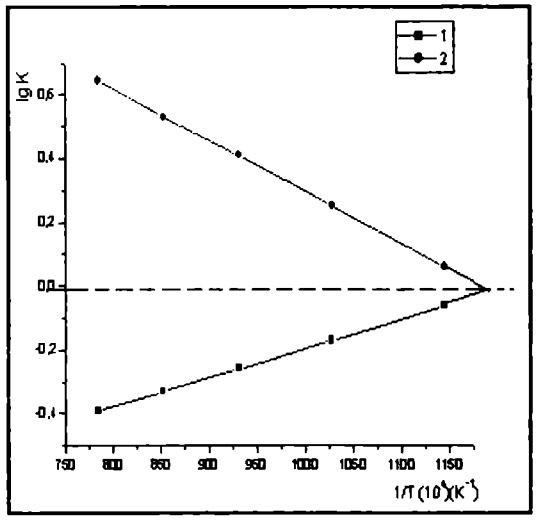
Solution

$\lg K = -\frac{\Delta H}{2.303RT} + C$ is the equation of a straight line in the graph $\lg K = f(1/T)$. Since the equilibrium conditions have the same form $K = P_{CO_2} / P_{CO}$ there is only one temperature at which both reactions could be in equilibrium simultaneously, the temperature at which $K_1 = K_2$. We plot $\lg K_1$ versus $1/T$ and $\lg K_2$ versus $1/T$ on the same graph. The intersection point gives $1/T = 11.95 \cdot 10^4$ and T = 840.3 K and $\lg K_1 = \lg K_2 = -0.01$.



2.6.2.5. In the table there are $\Delta H^f_{298}, \Delta G^f_{298}$ and C^0_P for substances:

	CO (g)	CO_2 (g)	Pb (s)	PbO (s)
ΔH^f_{298} (kcal mole^{-1})	-26.42	-94.05	0	-52.40
ΔG^f_{298} (kcal mole^{-1})	-32.81	-94.26	0	-45.25
C^o_P (cal K^{-1} mole^{-1})	6.95	8.76	6.34	11.07

Assume that the heat capacities are constant between 25 and 127^{0}C.

(a) Find ΔH^o, ΔG^o, and K_p at 25^{0}C for the reaction

PbO (s) + CO (g) ⇆ Pb (s) + CO_2 (g)

(b) Express ΔH^o as a function of temperature, valid for all temperatures between 25 and 127^{0}C.

(c) Find K_P at 127^{0}C.

Solution

(a) $\Delta H^o_{298} = 0 - 94.05 - (-52.40) - (-26.42) = -15.23$ kcal

$\Delta G^o_{298} = 0 - 94.26 - (-45.25) - (-32.81) = -16.20$ kcal

$\lg K_p = \frac{-\Delta G^o}{2.303RT} = \frac{16.20}{4.576 \times 10^{-3} \times 298} = 11.88$

$K_p = 7.6 \times 10^{11}$

(b) $\Delta C^o_p = 6.34 + 8.76 - 11.07 - 6.95 = -2.92$ cal K^{-1} mole^{-1}

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$$\Delta H_T^o = \Delta H_{298}^o + \int_{298}^{T} \Delta C_p^o dT$$

$$= -15.23 - 2.92 \times 10^{-3} \times (T - 298) \text{ kcal}$$

$$= -14.36 - 2.92 \times 10^{-3} T \text{ kcal}$$

(c) $$\lg K_{p,400} = \lg K_{p,298} + \frac{1}{2.303R} \int_{298}^{400} \frac{\Delta H_T^o}{T^2} dT$$

$$= 11.88 + \frac{1}{4.576 \times 10^{-3}} \times \int_{298}^{400} \left(\frac{-14.36}{T^2} - \frac{2.92 \times 10^{-3}}{T} \right) dT$$

$$= 11.88 + \frac{1}{4.576 \times 10^{-3}} \times \left[\frac{-14.36(400 - 298)}{400 \times 298} - 2.92 \times 10^{-3} \ln \frac{400}{298} \right] = 7.32$$

$K_p = 2.1 \text{ x } 10^7$

2.6.2.6. In the table there are ΔH^o (kcal) and ΔG^o (kcal) for reactions:

at 300 K	ΔH^o (kcal)	ΔG^o (kcal)
2 $(CH_2OH)_2$ (l) + 5 O_2 (g) ⇆ 4 CO_2 g) + 6 H_2O (l)	-546.96	-562.94
C (graphite) + O_2 (g) → CO_2 (g)	-94.05	-94.26
2 H_2 (g) + O_2 (g) → 2 H_2O (l)	-136.64	-113.38

	C (graphite)	H_2	O_2	CO_2	H_2O (l)	$(CH_2OH)_2$ (l)
C_p^o (cal K^{-1} $mole^{-1}$)	2.04	6.84	6.98	8.76	17.98	35.45

Assume that all gases are ideal and that each C_p^o is constant between 280 and 370 K.

For the reaction

2 C (graphite) + 3 H_2 + O_2 → $(CH_2OH)_2$ (l), find

(a) ΔH^o at 300 K.

(b) ΔG^o at 300 K.

(c) ΔE^o at 300 K.

(d) ΔF^o at 300 K.

(e) ΔH^o as a function of temperature. For what range of temperature is the expression valid?

(f) ΔH^o at 350 K.

(g) K_P (or log K_P) at 300 K.

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(h) Explain the significance of the superscript ° (as in ΔH^o, not as in 300°). Indicate and explain in which of the above cases the omission of this superscript would be a serious error.

Solution

	(a) ΔH^o_{300}	(b) ΔG^o_{300}
$2\ CO_2\ (g) + 3\ H_2O\ (l) \rightarrow (CH_2OH)_2 + 5/2\ O_2\ (g)$	273.48	281.47
$2\ C\ (graphite) + 2\ O_2\ (g) \rightarrow 2\ CO_2\ (g)$	-188.10	-188.52
$3\ H_2\ (g) + 3/2\ O_2\ (g) \rightarrow 3\ H_2O\ (l)$	-204.96	-170.07
	(a) −119.58 kcal	(b) −77.12 kcal

(c) $\Delta E^o = \Delta H^o - RT\Delta n_{gas}$

$$= -119.58 - 1.987 \times 10^{-3} \times 300(-4) = -117.20 \text{ kcal}$$

(d) $\Delta F^o = \Delta G^o - RT\Delta n_{gas} = -74.74 \text{ kcal}$

(e) $\Delta C_P^o = 35.45 - 2(2.04) - 3(6.84) - 6.98 \ = 3.87 \times 10^{-3}$ kcal K^{-1}

$$\Delta H_T^o = \Delta H_{300}^o + \int_{300}^{T} \Delta C_P^o dT = -119.58 + 3.87 \times 10^{-3}(T - 300) \text{ kcal}, \ 280 \le T \le 370 \text{ K}$$

(f) $\Delta H_{350}^o = -119.58 + 3.87 \times 10^{-3} \times 50 = -119.39 \text{ kcal}$

(g) $$\log K_p = \frac{-\Delta G^o}{2.303RT} = \frac{77.12}{2.303 \times 1.987 \times 10^{-3} \times 300} = 56.2$$

(h) The superscript ° indicates that an ideal gas is at 1.00 atm and that a solid or liquid is pure and under 1.00 atm pressure. E and H are insensitive to pressure or dilution and there is usually not much difference between E and E^o, or between H and H^o. However, F and G are very sensitive to pressure in case of a gas:

$$\left(\frac{\partial G}{\partial P}\right)_T = V, \ \left(\frac{\partial F}{\partial P}\right)_T = -P\left(\frac{\partial V}{\partial P}\right)_T$$

Thus, F^o or G^o (for 1 atm) is very different from F or G at some other pressure. For a liquid or a solid, however, V is small and thus F and G are insensitive to pressure. The serious difference in these cases would be between G^o (or F^o) for the pure substance and G (or F) for one component in a solution.

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2.6.2.7. Using the ΔH^o, S^o and C_P^o from table

	ΔH^o (kcal mole^{-1})	S^o (cal K^{-1} mole^{-1})	C_P^o (cal K^{-1} mole^{-1})
H_2 (g)	0	53.29	6.84
HCl (g)	-22.06	44.62	7.07
Na (s)	0	12.2	6.79
NaCl (s)	-98.23	17.30	12.11

(a) Find the equilibrium constant K_p for the reaction

NaCl (s) + ½ H_2 (g) ⇆ Na (s) + HCl (g)

as a function of temperature.

(b) Find K_p at 25^{0}C.

(c) Find the partial pressure of HCl at equilibrium at 25^{0}C in the presence of Na (s), NaCl (s) and H_2 (g, 4 atm). Assume that the gases are ideal.

Solution

(a) $\Delta H^o_{298} = -22.06 - (-98.23) = 76.17$ kcal

$$\Delta S^o_{298} = 44.62 + 12.2 - 17.30 - \frac{1}{2}(53.29) = 12.88 \text{ cal K}^{-1}$$

$$\Delta C_P^o = 6.97 + 7.07 - 12.11 - \frac{1}{2}(6.84) = 1.67 \text{ cal K}^{-1}$$

$$\Delta H_T^o = \Delta H^o_{298} + \Delta C_P^o (T - 298) = 76.17 - 1.67 \cdot 10^{-3}(T - 298) = 76.670 - 1.67T \text{ (cal)}$$

$$\Delta S_T^o = \Delta S^o_{298} + \Delta C_P^o \ln\frac{T}{298} = 12.9 - 1.67 \ln\frac{T}{298} = 22.4 - 1.67 \ln T \text{ cal K}^{-1}$$

$$\log K_p = -\frac{-\Delta G^o}{2.303RT} = \frac{1}{2.303R}\left(\frac{-\Delta H^o}{T} + \Delta S^o\right)$$

$$= \frac{1}{4.576}\left(\frac{-76{,}670}{T} + 1.67 + 22.4 - 1.67 \ln T\right) = \frac{-16{,}760}{T} + 5.26 - 0.840 \log T$$

(b) $T = 298^o K$

$$\log K_p = -51.39$$

$$K_p = 4.1 \times 10^{-52}$$

(c) NaCl (s) + ½ H_2 (g) ⇆ Na (s) + HCl (g)

$$K_p = \frac{P_{HCl}}{P_{H_2}^{1/2}}; \quad \frac{P_{HCl}}{4.00^{1/2}} = 4.1 \times 10^{-52}$$

$$P_{HCl} = 8.2 \times 10^{-52} \text{ atm}$$

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2.6.2.8. For the reaction 2 Hg (g) + O_2 (g) ⇆ 2 HgO (s) at 600 K, $\Delta H^o = -71.5$ kcal and $\Delta S^o = -91.9$ cal K^{-1} $mole^{-1}$. The heat capacities at constant pressure are:

O_2 (g)	6.31 + 0.0023 T (cal K^{-1} $mole^{-1}$)
HgO (s)	6.24 + 0.016 T (cal K^{-1} $mole^{-1}$)

(a) Assuming that the gases are ideal, what is C_P for Hg (g)?

(b) Find the equilibrium constant K_p for this reaction at 600 K.

(c) Calculate K_p at 300 K.

Solution

(a) $C_P = \frac{5}{2}R = 4.97$ cal K^{-1} $mole^{-1}$ for a monoatomic ideal gas

(b) $\Delta G^o_{600} = \Delta H^o_{600} - T\Delta S^o_{600} = -71.5 - 600(-919\times10^{-3}) = -16.4$ kcal

$$\lg K_p = -\frac{\Delta G^o_{600}}{2.303RT} = \frac{16.4}{4.576\times10^{-3}\times600} = 5.97$$

$$K_p = 9.3\times10^5$$

(c) $\Delta C_p = 2(6.24 + 0.016T) - 2(4.97) - (6.31 + 0.0023T) = -3.77 + 0.0297$ cal K^{-1}

$$\Delta H^o_{300} = \Delta H^o_{600} + \int_{600}^{300}\Delta C_P dT = -71.5 - 3.77\times10^{-3}(300-600) + \frac{1}{2}\times2.97\cdot10^{-5}(300^2 - 600^2)$$

$$= -74.4 \text{ kcal}$$

$$\Delta S^o_{300} = \Delta S^o_{600} + \int_{600}^{300}\frac{\Delta C_P}{T}dT = -91.9 + \int_{600}^{300}\left(-\frac{3.77}{T} + 0.0297\right)dT$$

$$= -91.9 - 3.77\ln\frac{300}{600} + 0.0297(300-600) = -98.2 \text{ cal } K^{-1}$$

$$\Delta G^o_{300} = \Delta H^o_{300} - T\Delta S^o_{300} = -74.4 - 300(-98.2\cdot10^{-3}) = -44.9 \text{ kcal}$$

$$\lg K_p = -\frac{\Delta G^o}{2.303RT} = \frac{44.9}{4.576\cdot10^{-3}\cdot300} = 32.7$$

$$K_p = 5\cdot10^{32}$$

2.6.2.9. At 300 K, the equilibrium constant K_p for reaction

N_2O_4 (g) ⇆ 2 NO_2 (g) is 0.174.

Calculate the mole fractions of N_2O_4 and NO_2 formed by the dissociation of pure N_2O_4 at a total pressure of 1 atm at this temperature.

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Solution

N_2O_4 (g) ⇆ 2 NO_2

(1 - α) 2 α moles at equilibrium

Total number of moles at equilibrium = 1 + α

$$K_p = \frac{\left(\frac{2\alpha}{1+\alpha}\right)\times 1^2}{\left(\frac{1-\alpha}{1+\alpha}\right)\times 1} = 0.174$$

$$\frac{4\alpha^2}{1-\alpha^2} = 0.174\,, \quad \alpha = 0.204$$

$$\chi_{N_2O_4} = \frac{1-\alpha}{1+\alpha} = 0.661$$

$$\chi_{NO_2} = 0.339$$

2.6.2.10. The values of ΔG^o at 1396 K for reactions are:

(I) CO + H_2O ⇆ CO_2 + H_2 $\Delta G_I^o = 2290$ cal

(II) 2 CO + O_2 ⇆ 2 CO_2 $\Delta G_{II}^o = -75500$ cal

(a) Find the equilibrium constant of the reaction

(III) 2 H_2 + O_2 ⇆ 2 H_2O (g)

(b) and calculate the degree of H_2O dissociation at P = 0.1 atm.

Solution

(a) According to Hess's law:

(III) = (II) – 2 (I) and

$$\Delta G_{III}^o = \Delta G_{II}^o - 2\Delta G_I^o = -75500 - 4580 = -80130 \text{ cal}$$

Knowing the value of ΔG_{III}^o we can find K_{III}

$$\Delta G_{III}^o = -RT\ln K_{III}\,; \quad K_{III} = e^{\frac{-\Delta G_{III}^o}{RT}} = 3.5\times 10^{12}$$

(b) Let us express the equilibrium constant of the reaction of steam formation through the degree of dissociation α:

2 H_2O (g) + O_2 (g) = 2 H_2O (g)

2 α α 2(1-α)

The total number of moles at equilibrium is 2 + α.

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The partial pressures of components of the system are:

$$P_{H_2} = \frac{2\alpha}{2+\alpha} \times P; \quad P_{O_2} = \frac{\alpha}{2+\alpha} \times P; \quad P_{H_2O} = \frac{2(1-\alpha)}{2+\alpha} \times P$$

Inserting these expressions into K_p equation, we get

$$K_p = \frac{P_{H_2O}^2}{P_{H_2}^2 \cdot P_{O_2}} = \frac{\frac{4(1-\alpha)^2}{(2+\alpha)^2} P^2}{\frac{4\alpha^2}{(2+\alpha)^2} P^2 \times \frac{\alpha}{2+\alpha} P} = \frac{(1-\alpha)^2(2+\alpha)}{P\alpha^3}$$

This equation is a cubic one with respect to α. It requires a simple form when the degree of formation is very small (for steam at $T \leq 1500^0$C). In this instance the quantity α may be deleted in the parentheses of the nominator and we obtain

$$K_p = \frac{2}{P\alpha^3} \; ; \; \alpha = \sqrt[3]{\frac{2}{P \cdot K_p}}$$

$$\alpha = \sqrt[3]{\frac{2}{3.5 \cdot 10^{12} \cdot 0.1}} = \sqrt[3]{\frac{2}{0.35}} \cdot 10^{-4} = 1.784 \cdot 10^{-4}$$

2.6.2.11. (a) For the reaction

2 Ag (s) + 2 HCl (g) ⇆ 2 AgCl (s) + H_2 (g)

find ΔH^o, ΔG^o and K_p at 25^{0}C using the following data:

	HCl (g)	AgCl (s)
ΔH^f_{298} (kcal mole^{-1})	-22.06	-30.36
ΔG^f_{298} (kcal mole^{-1})	-22.77	-26.22

(b) Silver and silver chloride are placed in an evaporated flask. Hydrogen chloride is introduced at 25^{0}C until the pressure is 0.5 atm. The content of flask is then allowed to come to equilibrium at total pressure of 0.5 at and 25^{0}C. Some of each solid is still present and in contact with the gas at equilibrium. Find the partial pressure of HCl and H_2 in equilibrium mixture consider the gas to be ideal.

(c) Assume that the following molar heat capacities are constant between 0 and 50^{0}C.

	Ag	AgCl	H_2	HCl
C_P (cal K^{-1} mole^{-1})	6.01	12.61	6.80	7.09

Express ΔH^o as a function of temperature between 0 and 50^{0}C.

(d) Express lg K_p as a temperature function in the same interval.

(e) Find K_p at 50^{0}C.

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Solution

(a) $\Delta H^o_{298} = 2(-30.36) - 2(-22.06) = -16.60$ kcal

$\Delta G^o_{298} = 2(-26.22) - 2(-22.77) = -6.90$ kcal

$$\lg K = -\frac{\Delta G^o}{2.303RT} = \frac{6.90}{2.303 \times 1.987 \cdot 10^{-3} \cdot 298} = 5.06$$

$$K = 1.1 \times 10^5$$

(b) Ag (s) + 2 HCl (g) ⇆ 2 AgCl (s) + H_2 (g)

$n_0(1 - 2\alpha)$ $n_0\alpha$

$n_{total} = n_0(1 - \alpha)$

$$P_{H_2} = \left(\frac{\alpha}{1-\alpha}\right)(0.50) \text{ atm} \; ; \; P_{HCl} = \left(\frac{1-2\alpha}{1-\alpha}\right)(0.50) \text{ atm}$$

$$K_p = \frac{P_{H_2}}{P^2_{HCl}}$$

$$\frac{\alpha(1-\alpha)}{(1-2\alpha)^2(0.50)} = 1.1 \times 10^5$$

Let us introduce β as $\beta = 1 - 2\alpha$

Then $\alpha = ½ (1 - \beta)$, $1 - \alpha = ½ (1 + \beta)$

$$\frac{1-\beta^2}{\beta^2} = 2.2 \times 10^5 \; ; \; \beta = 2.1 \times 10^{-3}$$

$$P_{HCl} = \frac{0.50\beta}{1/2(1+\beta)} = 2.19 \times 10^{-3} \text{ atm}$$

$$P_{H_2} = \frac{1/2(1-\beta)(0.50)}{1/2(1+\beta)} = 0.50 \text{ atm}$$

(c) $\Delta C^o_p = 2 \times 12.61 + 6.80 - 2 \times 6.01 - 2 \times 7.09 = 5.82$ cal K^{-1} $mole^{-1}$

$$\Delta H^o_T = \Delta H^o_{298} + \int_{298}^{T} \Delta C^o_p dT$$

$$= -16.60 + 5.82 \times 10^{-3}(T - 298) = -18.49 + 5.82 \cdot 10^{-3} T \text{ kcal}$$

(d) $$\ln K = \ln K_{298} + \int_{298}^{T} \frac{\Delta H^o}{RT^2} dT$$

$$= \ln K_{298} + \frac{1}{R} \int_{298}^{T} \frac{-18.49 + 5.82 \times 10^{-3} T}{T^2} dT = 5.06 - \frac{18.49}{1.987} \int_{298}^{T} \frac{dT}{T^2} + \frac{5.82 \times 10^{-3}}{1.987} \int_{298}^{T} \frac{dT}{T}$$

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$$= 5.06 + 9.3054\left[\frac{1}{T} - \frac{1}{298}\right] + 2.929 \cdot 10^{-3}[\ln T - \ln 298]$$

$$= 5.06 - 0.03122 + \frac{9.3054}{T} + 2.929 \cdot 10^{-3} \ln T - 0.01668$$

$$= 5.012 + \frac{9.3054}{T} + 2.929 \cdot 10^{-3} \ln T$$

$$\ln K_{p_{325}} = 5.0150 + 0.0286 + 0.01694 = 5.0605$$

$$K_{325} = 157.66$$

2.6.2.12. Zinc oxide was left in contact with carbon monoxide, initially pure, at 1300 K and a total pressure of 1 *atm* until the reaction

Zn O (s) + Co (g) ⇆ Zn (g) + CO_2 (g)

had reached equilibrium. The density of the gas mixture was then 0.344 $g\ l^{-1}$. Find (a) the fraction of the CO that had reacted with ZnO, (b) the equilibrium constant K_P for the reaction.

Solution

(a) ZnO (s) + CO (g) ⇆ Zn (g) + CO_2 (g)

$n_0(1-\alpha)$ $n_0\alpha$ $n_0\alpha$

$n_{total} = n_0(1+\alpha)$ at equilibrium

The total weight of the gases is

$m = n_0 [(1-\alpha) \times 28 + \alpha \times 65.37 + \alpha \times 44] = n_0(28 + 81.37\alpha)$

$$M = \frac{m}{n_{total}} = \frac{28 + 81.37\alpha}{1+\alpha} = 36.7 \text{ because}$$

$$M = \frac{\rho RT}{P} = 0.344\ g\ l^{-1}\ \frac{0.082 l\ atm \cdot K^{-1} mole^{-1}}{1 \cdot atm} \times 1300\ K = 36.7\ g\ mole^{-1}$$

And $\alpha = 0.1947$

(b) $P_{CO_2} = P_{Zn} = \frac{n_0\alpha}{n_0(1+\alpha)} \cdot P = 0.1629\ atm$; $P_{CO} = \frac{1-\alpha}{1+\alpha} \cdot P = 0.674\ atm$

$$K_P = \frac{P_{CO_2} \cdot P_{Zn}}{P_{CO}} = 3.93 \times 10^{-2}\ atm.$$

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2.6.2.13. In the reaction $AB_2 = A + 2B$ all three substances are ideal gases. A 10 liter flask contains, initially, 0.4 *moles* of AB_2. A catalyst for dissociation is then introduced. When equilibrium is attained, the pressure of the mixture is 1.20 *atm*. The temperature is 300 K. Find the equilibrium constant K_P.

Solution

$AB_2 \leftrightarrows A + 2B$

$(0.4-\alpha) \quad \alpha \quad 2\alpha$ *moles* at equilibrium

$n_{total} = 0.4 + 2\alpha$

$$n = \frac{PV}{RT} = \frac{1.20atm \times 20l}{0.082latmmole^{-1}K^{-1} \times 300K} = 0.487\ moles$$

$0.4 + 2\alpha = 0.487 \quad \alpha = 0.044$

$$K_P = \frac{P_A \cdot P_B^2}{P_{AB_2}} = \frac{\frac{\alpha}{0.4+\alpha} \times P \times \frac{4\alpha^2}{(0.4+\alpha)^2} \times P^2}{\left(\frac{0.4-\alpha}{0.4+\alpha}\right) \times P} = \frac{4\alpha^3 \cdot P^2}{(0.4-\alpha)(0.4+\alpha)^2} = 6.99 \cdot 10^{-3} atm^2$$

2.6.2.14. In the reaction $2\ SO_2 + O_2 \leftrightarrows 2\ SO_3$, 0.1 *mole* of SO_2 and SO_3 are mixed in a 2 liter flask at 27°C. After equilibrium is attained, the pressure is 2.78 *atm*.

Calculate: (a) the *mole* fraction of O_2 at equilibrium and (b) K_P.

Solution

(a) $2\ SO_2 + O_2 \leftrightarrows 2\ SO_3$

$(0.1-2\alpha) \quad \alpha \quad (0.1+2\alpha)$ *moles* at equilibrium

$n_{total} = 0.2 + \alpha$

$$n = \frac{PV}{RT} = \frac{2.78atm2l}{0.082latmK^{-1}mole^{-1} \times 300K} = 0.226\ mole;\ \alpha = 0.026$$

$$x_{O_2} = \frac{n_{O_2}}{n_{total}} = \frac{0.026}{0.226} = 0.115$$

$$(b)\ K_P = \frac{P_{SO_3}^{\ 2}}{P_{SO_2}^2 \cdot P_{O_2}} = \frac{n_{SO_3}^{\ 2}}{n_{SO_2}^2 \cdot n_{O_2}} \cdot \frac{1}{P} = \frac{n_{SO_3}^{\ 2}}{n_{SO_2}^2 \cdot n_{O_2}} \cdot \frac{V}{RT} =$$

$$= \frac{0.152}{0.048^2 \cdot 0.026} \cdot \frac{2l}{0.082l \cdot atm \cdot K^{-1}mole^{-1} \cdot 300K} = 31.35\ atm^{-1}$$

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2.6.2.15. For the reaction Br_2 (l) + Cl_2 (g) ⇆ 2 BrCl (g), K_P = 2.032 at 25°C. The vapor pressure of Br_2 (l) at 25°C is 0.281 *atm*. Pure BrCl (g) was introduced into a closed container of adjustable volume. The total pressure was kept constant at 1.000 *atm* and the temperature at 25°C. Br_2 (l) was present at equilibrium. Find the fraction of BrCl originally present that has been converted to Br_2 and Cl_2 at equilibrium. Assume that the gases are ideal.

Solution

2 BrCl ⇆ Br_2 (l) + Cl_2 (g)

$$K_P = \frac{1}{2.032} = 0.4921$$

$P_{BrCl} + P_{Cl_2} = 1.000 - 0.281 = 0.719\ atm$

Let n_0= the number of *moles* of BrCl initially present. At equilibrium

$n_{BrCl} = n_0 (1-\alpha)$

$n_{Cl_2} = n_0 \times \frac{1}{2}\alpha \quad (1BrCl \rightarrow \frac{1}{2} Cl_2)$

$n_{BrCl} + n_{Cl_2} = n_0 (1 - \frac{1}{2}\alpha)$

$$P_{BrCl} = \frac{n_0(1-\alpha)}{n_0(1-\frac{1}{2}\alpha)} \times 0.719 atm$$

$$P_{Cl_2} = \frac{n_0 \times \frac{1}{2}\alpha}{n_0(1-\frac{1}{2}\alpha)} \times 0.719 atm$$

$$\frac{P_{Cl_2}}{P_{BrCl}^2} = \frac{\frac{1}{2}\alpha\left(1-\frac{1}{2}\alpha\right)}{(1-\alpha)^2 \times 0.719} = .4921$$

$0.604\alpha^2 - 1.208\alpha + 0.354 = 0$; $\alpha = 0.357$

2.6.2.16. The equilibrium constant for the reaction Fe_3O_4 (s) + CO (g) ⇆ 3FeO (s) + CO_2 (g) is 1.15 at 600°C. If a mixture consisting initially of 1 *mole* of Fe_3O_4, 2 *moles* of CO, 0.5 *moles* of FeO and 0.3 *moles* of CO_2 were heated to 600°C at constant total pressure of 5.00 *atm* what would be the amount of each substance at equilibrium.

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Solution

Fe_3O_4 (s) + CO (g) ⇆ 3FeO (s) + CO_2 (g)

1-y 2-y (0.5+3y) (0.3+y) *moles* at equilibrium

Total number of *moles* of gas = 2.3

$$P_{CO} = \frac{2-y}{2.3} \times 5 ; P_{CO_2} = \frac{0.3+y}{2.3} \times 5 ;$$

$$K_P = \frac{P_{CO_2}}{P_{CO}} = \frac{0.3+y}{2-y} = 1.15 \quad y=0.93$$

Number of *moles*, at equilibrium, of CO_2 is 1.23; of CO is 1.07; of Fe_3O_4 is 0.07 and of FeO is 3.29.

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2.7. THE THERMODYNAMICS OF REAL GAS

2.7.1. For an ideal gas (or a real gas at 0 pressure), which of the following is true?

(a) f = P; (b) $\gamma = 1$, (c) f/P = 0, (d) f/P =0, (d) f/P = f/0 = ∞, (e) $\gamma = 0$.

Solution

(a) and (b).

2.7.2. Evaluate lnγ for a gas that has the equation of state P(V-b) = RT

Solution

$$V = b + \frac{RT}{P}\,;\quad \left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{V}{RT}$$

$$d\ln\gamma = d\ln\left(\frac{f}{P}\right)$$

$$\left(\frac{\partial \ln f/P}{\partial P}\right)_T = \frac{\partial \ln f}{\partial P} - \frac{\partial \ln P}{\partial P} = \frac{V}{RT} - \frac{1}{P} = \frac{b + \frac{RT}{P}}{RT} - \frac{1}{P} = \frac{b}{RT} + \frac{1}{P} - \frac{1}{P} = \frac{b}{RT}$$

$$d\ln\gamma = d\ln\left(\frac{f}{P}\right) = \frac{b}{RT}dP$$

$$\ln\gamma = \int_{\gamma=1}^{\gamma} d\ln\gamma = \frac{1}{RT}\int_0^P bdP = \frac{bP}{RT}$$

2.7.3. For helium,B in the equation of state PV = RT + BP is essentially constant and equals 11.5 $cm^3\ mole^{-1}$ in the range 30 –90 °C. Find (a) an expression for γ and its value at P = 1 atm and 60°C; (b) expression and value of Joule-Thompson enthalpy.

Solution

(a) $\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{V}{RT}$. From equation of state: $V = B + \frac{RT}{P}$

$$\left(\frac{\partial \ln f/P}{\partial P}\right)_T = \left(\frac{\partial \ln f}{\partial P}\right)_T - \left(\frac{\partial \ln P}{\partial P}\right)_T$$

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$$\frac{\partial \ln f/P}{\partial P} = \frac{V}{RT} - \frac{1}{P} = \frac{1}{RT}\left(V - \frac{RT}{P}\right) = \frac{B}{RT}$$

$$d\ln\frac{f}{P} = \frac{B}{RT}dP; \quad \int_0^{\ln\frac{f}{P}} d\ln\frac{f}{P} = \int_0^{P}\frac{B}{RT}dP$$

$$\ln\frac{f}{P} - \ln\left(\frac{f}{P}\right)_{\substack{P\to 0\\ f\to 1}} = \frac{B}{RT}\cdot P$$

$$\ln\gamma = \frac{BP}{RT} = \frac{11.5\cdot 10^{-3}\,mole^{-1}\cdot 1atm}{0.082l\cdot atm\cdot mole^{-1}K^{-1}\cdot 333K} = 0.42\cdot 10^{-3}$$

$\gamma = 1.0004$

(b) $$\left[\frac{\partial \ln(f/P)}{\partial T}\right]_P = \left(\frac{\partial \ln f}{\partial T}\right)_P = \frac{\partial}{\partial T}\left(\frac{BP}{RT}\right)_P = -\frac{BP}{RT^2} = -\frac{\Delta H}{RT^2}$$

$\Delta H = BP = 11.5 \cdot cm^3\ mole^{-1} \cdot 1\ atm$

$$= 11.5 \cdot 10^{-3}\ l\ atm\ mole^{-1} \cdot \frac{1.987 cal\cdot mole^{-1}K^{-1}}{0.082 l\cdot atm\cdot mole^{-1}K^{-1}} = 0.278\ cal\ mole^{-1}$$

2.7.4. For N_2O at 0°C fugacity coefficient $\gamma = \frac{f}{P}$ is 0.9847 at 2 atm and 0.6961 at 60 atm. Evaluate ΔG in calories for the isothermal compression of 1 mole of this substance from 3 to 60 atm at 0°C.

(a) assuming ideal gas behaviour

(b) using the fugacity data

Solution

(a) $$\Delta G = \int_{P_1}^{P_2} VdP = RT\ln\frac{P_2}{P_1} = 1.987\times 273.2\times 2.303\lg\frac{60}{3} = 1628\ cal$$

(b) $$\Delta G = RT\ln\frac{f_2}{f_1} = 1.987\times 2.303\times 273.2\lg\left(\frac{60\times 0.6961}{3\times 0.9847}\right) = 1440\ cal$$

2.7.5. A gas has the equation of state

$PV = RT + aP^{1/2} + bP + cP^{3/2}$

Derive an equation relating the fugacity coefficient, γ, to the pressure at constant temperature.

Solution

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We introduce $\alpha = V - \frac{RT}{P}$

$$\left(\frac{\partial \ln \frac{f}{P}}{\partial P}\right)_T = \left(\frac{\partial \ln f}{\partial P}\right)_T - \left(\frac{\partial \ln P}{\partial P}\right)_T = \frac{V}{RT} - \frac{1}{P} = \frac{1}{RT}\left(V - \frac{RT}{P}\right)$$

$$\left(\frac{\partial \ln \gamma}{\partial P}\right)_T = \frac{\alpha}{RT}\,;\ \mathrm{d}\ln\gamma = \frac{\alpha}{RT}dP$$

From above equation of state

$$V = \frac{RT}{P} + aP^{-1/2} + b + cP^{1/2}$$

$$\alpha = \frac{RT}{P} + aP^{-1/2} + b + cP^{1/2} - \frac{RT}{P} = b + aP^{-1/2} + cP^{1/2}$$

$$\ln\gamma = \int_0^{\ln\gamma} d\ln\gamma = \frac{1}{RT}\int_0^P \left(b + aP^{-1/2} + cP^{1/2}\right)dP$$

$$= \frac{1}{RT}\left(bP + 2aP^{-1/2} + \frac{2}{3}cP^{3/2}\right)$$

2.7.6. A gas has the equation of state $V = \frac{RT}{P}\left(1 + AP + BP^2\right)$ where A and B are function of temperature.

Find the fugacity coefficient, γ, in terms of the quantities P, A and B.

Solution

$$\frac{V}{RT} = \frac{1}{P} + A + BP$$

$$\left(\frac{\partial \ln \frac{f}{P}}{\partial P}\right)_T = \left(\frac{\partial \ln f}{\partial P}\right)_T - \frac{\partial \ln P}{\partial P} = \frac{V}{RT} - \frac{1}{P}$$

$$\mathrm{d}\ln\gamma = \left(\frac{V}{RT} - \frac{1}{P}\right)dP$$

$$\ln\gamma = \int_0^P \left(\frac{V}{RT} - \frac{1}{P}\right)dP = \int_0^P (A + BP)dP = AP + \frac{1}{2}BP^2$$

$$\gamma = \mathrm{e}^{AP + \frac{1}{2}BP^2}$$

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2.7.7. At 10.3 atm and -15°C the molar volume of N_2O is 1.8566 l. Estimate the fugacity coefficient for N_2O in these conditions.

Solution

$$V_{ideal} = \frac{RT}{P} = \frac{0.082 l \cdot atm \cdot mole^{-1} K^{-1} \cdot 258 K}{10.3 atm} = 2.0539$$

$$\alpha = V_{real} - V_{ideal} = 1.8566 - 2.0539 = -0.197\ l$$

$$\ln \gamma = \frac{1}{RT} \int_0^P \left(V - \frac{RT}{P} \right) dP = \frac{1}{RT} \int_0^P \alpha dP = -\frac{0.197 l \times 10.3 atm}{0.082 l \cdot atm \cdot K^{-1} \times 258 K}$$

$$\ln \gamma = 0.0959$$

$$\gamma = 1.1.$$

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2.8. HETEROGENEOUS PHASE EQUILIBRIUM

2.8.1. GIBBS' PHASE RULE

2.8.1.1. Indicate precisely the conditions under which the formula F = C - P + 2 is valid, where F is the number of degrees of freedom, C is number of the components of the system, P is number of phases and 2 are temperature and pressure.

Solution

The formula is valid for a system at equilibrium in which phase concentrations plus two other properties of state can be varied.

2.8.1.2. What would be the number of degrees of freedom in a system in which pure H_2O was raised to a temperatute sufficiently high to allow dissociation into H_2 and O_2 at constant pressure?

Solution

$2\ H_2O\ (l) \rightarrow 2H_2\ (g) + O_2\ (g)$

General equation of variance, F, is : F = (C - R) – P + 2 where R is the number of independent reaction between system components, C, in our case 3 – 1. Number of phases is P and 2 means two independent parameters : pressure and temperature. At constant – pressure:

F = (3 –1) – 2 + 1 = 2 – 2 + 1 = 1.

2.8.1.3. Calculate the number of components, C, of the system iceberg + water ocean + atmosphere, supposing that the atmosphere contains only water vapors.

Solution

C = 1.

2.8.1.4. Explain why the system KCl-NaCl-H_2O should be regarded as a 3 component system, whereas KCl-NaBr-H_2O should be regarded as a 4 component system.

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Solution

The number of components, C, is the number of possible species, N, minus the number of independent equations, R, relating their concentrations, mole fractions, etc. Each independent chemical equilibrium involving the constituents counts as one equation. The condition that a solution be electrically neutral counts as one if ions are considered constituents.

In the system

$KCl\text{-}NaCl\text{-}H_2O$

N = 3 (KCl, NaCl, H_2O), R = 0, C = 3

In the system

$KCl\text{-}NaBr\text{-}H_2O$

N = 5 (KCl, NaBr, NaCl, KBr, H_2O)

R = 1 (KCl + NaBr = NaCl + KBr), C = 5 –1 = 4

2.8.1.5. Determine the number of components for the following systems:

(a) NH_4Cl (c), NH_4^+(aq), Cl^-(aq), H_2O(l), H_3O^+(aq), H_2O(g), NH_3(g), OH^-(aq), NH_4OH(aq).

(b) NH_4Cl(c), NH_3(g), HCl(g), where the partial pressure of NH_3 is allways equal to the partial pressure of HCl as in the case where all the gas is formed by the sublimation of NH_4Cl (c).

(c) NH_4Cl (c), NH_3(g), HCl(g), where the partial pressure of NH_3(aq), is not necessarily equal to the partial pressure of HCl.

(d) CH_3COONH_4(c), CH_3COO^-(aq), NH_4^+(aq), H_3O^+(aq), NH_3(aq), OH^-(aq), CH_3COOH(aq), H_2O(l), H_2O(g), taking hydrolysis into account.

(e) NaCl(c), KBr(c), K+(aq), Na^+(aq), Cl^-(aq), Br^-(aq), H_2O(l), H_2O(g).

(f) NaCl(c), KCl(c), Na^+(aq), Cl^-(aq), H_2O(l), H_2O(g).

(g) $CaCl_2 \cdot 6H_2O$(c), Ca^{2+}(aq), Cl^-(aq), H_2O(l), H_2O(g).

(h) $CaCO_3$(c), CaO(c), CO_2(g) where all the CaO and CO_2 in the system are formed by the decomposition of $CaCO_3$(c).

Solution

(a) N = (NH_4Cl, NH_4^+, Cl^-, H_2O, NH_3, NH_4OH, H_3O^+, OH^-)

R = 4

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$NH_4Cl \leftrightarrows NH_4^+ + Cl^-$

$NH_4^+ + H_2O \leftrightarrows NH_3 + OH^-$

$NH_3 + H_2O \leftrightarrows NH_4OH$

$2H_2O \leftrightarrows H_3O^+ + OH^-$

$C = 8 - 4 = 4$

(b) N = 3 (NH_4Cl, NH_3, HCl)

R = 2 $NH_4Cl \leftrightarrows NH_3 + HCl$

$P_{NH3} = P_{HCl}$

$C = N - R = 3 - 2 = 1$

(c) N = 3 (NH_4Cl, NH_3, HCl)

R = 1 $NH_4Cl \leftrightarrows NH_3 + HCl$

$C = N - R = 3 - 1 = 2$

(d) N = 8 (CH_3COONH_4, CH_3COO^-, NH_4^+, H_3O^+, NH_3, OH^-, CH_3COOH, H_2O)

R = 4 $CH_3COOH + H_2O \leftrightarrows CH_3COO^- + H_3O^+$

$CH_3COO^- + H_2O \leftrightarrows CH_3COOH + OH^-$

$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$

$NH_3 + H_2O \leftrightarrows NH_4OH$

$C = N - R = 8 - 4 = 4$

The equation $2H_2O \leftrightarrows H_3O^+ + OH^-$ was not counted because it can be derived by addition of the first two equations.

(e) N = 9 (NaCl, KBr, KCl, NaBr, K+, Na^+, Cl^-, Br^-, H_2O)

R = 4 $NaCl \leftrightarrows Na^+ + Cl^-$

$KBr \leftrightarrows K^+ + Br^-$

$NaBr \leftrightarrows Na^+ + Br^-$

$NaCl + KBr \leftrightarrows NaBr + KCl$

electroneutrality

$C = N - R = 9 - 4 = 5$

(f) N = 6 (NaCl, NaBr, K+, Na^+, Cl^-, H_2O)

R = 2 $NaCl \leftrightarrows Na^+ + Cl^-$

$KCl \leftrightarrows K^+ + Cl^-$

electroneutrality

$C = N - R = 6 - 2 = 4$

(g) N = 4 ($CaCl_2 \cdot 6H_2O$, Ca^{2+}, Cl^-, H_2O)

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R = 2 $CaCl_2 \cdot 6H_2O \leftrightarrows Ca^{2+} + 2Cl^- + 6H_2O$
electroneutrality

C = N - R = 4 - 2 = 2

(h) N = 3 ($CaCO_3$, CaO, CO_2)

R = 1 $CaCO_3 \leftrightarrows CaO + CO_2$

C = N - R = 3 - 1 = 2

The restriction that CaO and CO_2 are present in stoichiometrically equal amounts does not count here because it does not affect a phase composition. No matter what the proportions, the composition of the gas phase is always 100 per CO_2 and the composition of the CaO phase is always 100 percent CaO.

2.8.1.6. Show that on the basis of slope sign there are 8 and only 8 possible unique configurations of the 2-phases lines around a triple point in one-component pressure-temperature diagram. Sketch them.

Solution

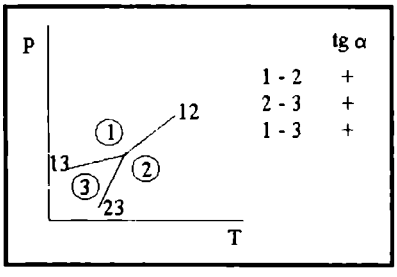
In pressure-temperature diagram, P = f (T), the slope means $\partial P/\partial T$ = tg α. The sign of tg α is :

	0-90	90-180	180-270	270-360
tg α	+	-	+	-

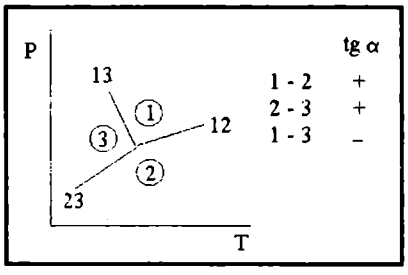
The slope of each line may be + or -.

Labelling the three phases 1, 2, 3, the possible permutations of these signs are:

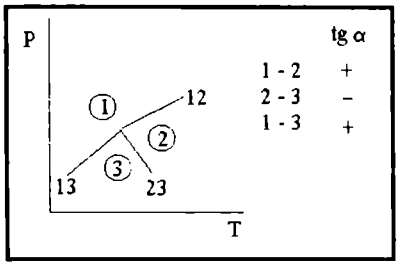
a)



b)



c)



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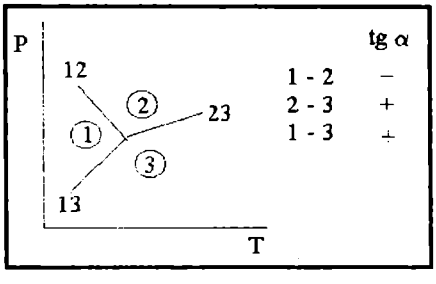

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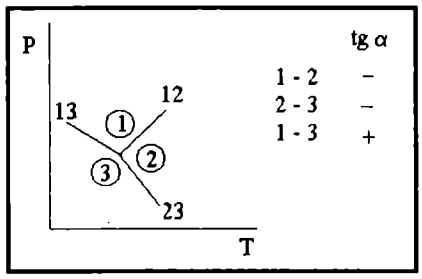
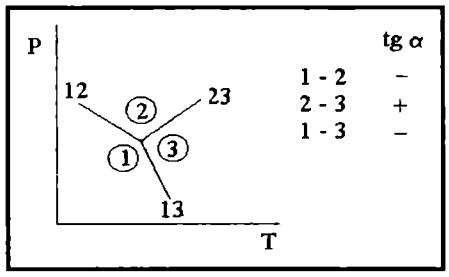
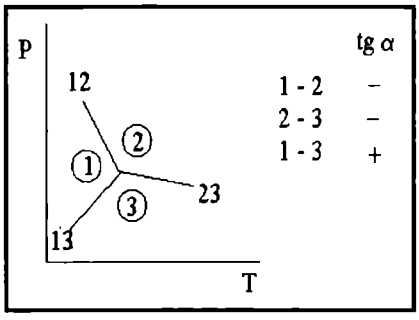
e)



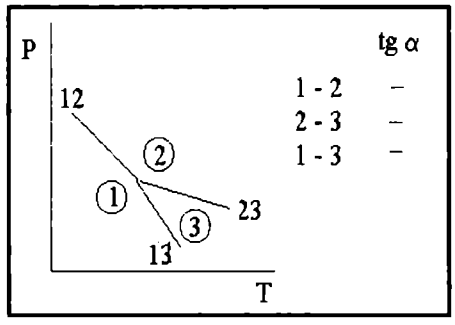
f)



g)



h)



2.8.1.7. A certain substance exists in two solid forms, Q and R, as well as liquid and vapor. The following triple points are observed: all equilibria are stable.

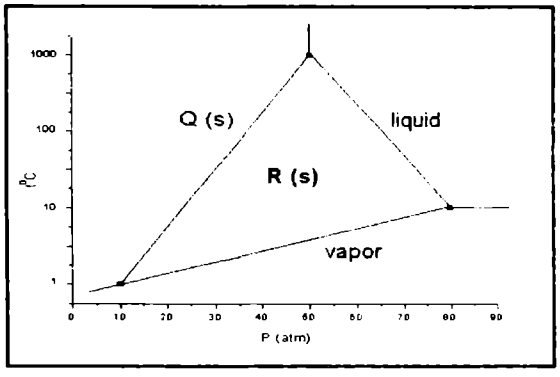
Temperature (°C)	Pressure (atm)	Phases
10	1.0	Q, R, vapor
50	1000.0	Q.R, liquid
80	10.0	R, liquid, vapor

(a) Sketch the P-T phase diagram and indicate phases present in each region

(b) In each pair select the form with greater density in the vicinity of 50°C and 100 atm if you have enough informations to decide: Q and R: R and liquid (l); Q and liquid. If you cannot decide, explain why not.

Solution

(a)



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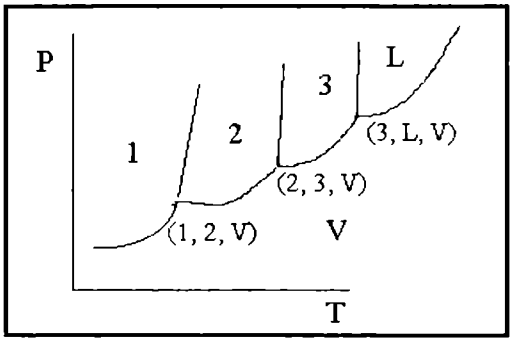
(b) Increasing the pressure, at constant temperature, favors the denser form in the order

$\rho_Q > \rho_R$; $\rho_l > \rho_R$

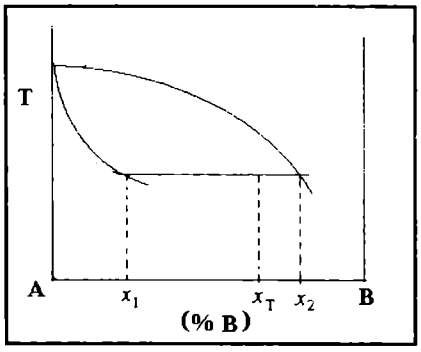
We cannot decide about Q and l because we do not know whether the Q-l equilibrium line has a positive or negative slope.

2.8.1.8. One element exists in the form of vapor, V, a liquid, L, and three allotropic modifications known as 1, 2 and 3. Complete the phase diagram in a logical manner and label all lines and areas. The triple points existing in the system are as follows: 1-2-V, 2-3-V and 3-L-V.

Solution



2.8.1.9.



For the system shown in the figure prove that at equilibrium

$$\frac{m_1}{m_2} = \frac{x_2 - x_T}{x_T - x_1}$$

where m_1 is the weight of phase 1, m_2 is the weight of phase 2, x_1 is the weight percent of B in phase 1, x_2 is the weight percent of B in phase 2 and x_T is the weight percent of B in the total system.

Solution

Let m_T = the total weight of the whole system.

Then $m_T x_T = m_1 x_1 + m_2 x_2$ and $m_T = m_1 + m_2$

$m_1 x_T + m_2 x_T = m_1 x_1 + m_2 x_2$

$m_1(x_1 - x_T) = m_2(x_2 - x_T)$; $\qquad \frac{m_1}{m_2} = \frac{x_2 - x_T}{x_T - x_1}$

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2.8.2. ONE COMPONENT SYSTEM: CLAPEYRON AND CLAUSIUS –CLAPEYRON EQUATIONS

2.8.2.1. Prove that the liquid-vapor (L-V) equilibrium graph in one-component system must always have a positive slope on a pressure-temperature diagram.

Solution

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{S_v - S_l}{V_v - V_l}$$

$S_v > S_l$ and $V_v > V_l$

Therefore $\frac{dP}{dT} = \frac{+}{+} = positive$.

2.8.2.2. Calculate (a) the entropy and (b) heat of vaporization of 1g of ethyl alcohol at 20°C if the pressure of the saturated vapor of the substance are:

temperature (°c)	pressure (mmHg)
19.5	42.64
20.0	43.80
20.5	44.96

The density of liquid ethyl alcohol is 0.7894 g cm^{-3}, that of the saturated vapor is 0.000111 g·cm^{-3}.

Solution

(a) The reciprocals of the densities (the specific volumes) are respectively 1.27 and 9010 cm^3 g^{-1}.

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}\ ;\ \Delta^v S = \Delta V \frac{dP}{dT}$$

$$\frac{dP}{dT} \cong \frac{\Delta P}{\Delta T} = \frac{(44.96 - 42.64)mmHg \cdot 1atm}{1K \cdot 760mmHg} = 0.003060\ \text{atm}\cdot K^{-1}$$

$\Delta^v S = (9010 - 1.27) \times 10^{-3} l \cdot g^{-1} \times 0.00306\ \text{atm}\ K^{-1} = 27.56 \cdot 10^{-3} l \cdot \text{atm} \cdot K^{-1} g^{-1}$

$$= 27.56 \times 10^{-3} \times \frac{1.987}{0.082}\ \text{cal}\ g^{-1}\ K^{-1} \times 46\ \text{g mole}^{-1} = 30.72\ \text{cal}\cdot \text{mole}^{-1}\ K^{-1}$$

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(b) $\frac{d\ln P}{dT} = \frac{\Delta^v H}{RT^2}$; $\Delta^v H = RT^2 \text{ x } \frac{1}{P} \times \frac{dP}{dT}$

$\Delta^v H = 1.987 \text{ x } (293.2)^2 \text{ x } \frac{0.00306}{43.8} \times 760 = 9{,}069.5 \text{ cal mole}^{-1}$.

2.8.2.3. Make a rough estimation of the molar enthalpy of vaporization of n-pentane. The normal boiling point is 36°C.

Solution

Trouton's rule is:

$\frac{\Delta^v H}{T_b} = 21 cal \text{ K}^{-1} \text{ mole}^{-1}$; $\Delta^v H = 21 \text{ T}_b = 21 \text{ x } 309 = 6500 \text{ cal mole}^{-1}$.

2.8.2.4. Estimate the pressure required to melt ice at –1.0°C. The specific heat of fusion of ice is 80 cal g^{-1}. The density of the liquid is 1.0 g cm^3, that of the solid is 0.92 g cm^{-3}.

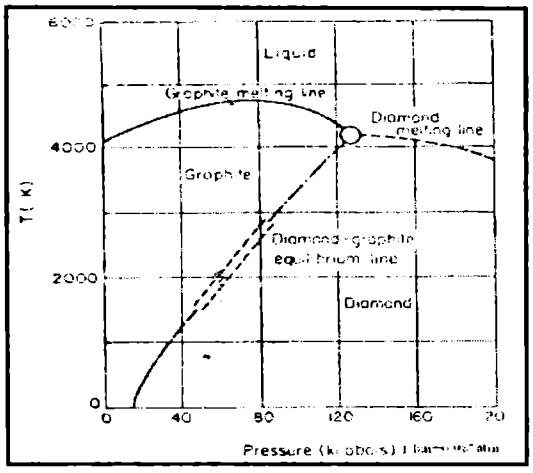
Solution

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} = \frac{80}{(273.2)[(0.92-1.0)]/(1.0\times 0.92)} = -3.36 \text{ cal cm}^{-3} \text{ K}^{-1}$$

$$\Delta P = -3.36 \times \Delta T = -3.36(-1) = 3.36 \frac{cal}{cm^3} = 3.36 \frac{cal}{10^{-3} l}$$

$$= 3.36 \frac{cal}{10^{-3} l} \cdot \frac{0.082 l \cdot atm}{1.987 cal} = 139 \text{ atm.}$$

2.8.2.5. The pressure-temperature diagram of carbon is:



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(a) What is the pressure to convert graphite into diamond at 2000 K?

(b) At any given temperature and pressure, which phase is denser, graphite or diamond?

(c) At which temperature and pressure do graphite and molten carbon have the same density?

Solution

(a) 60 kilobars = 60 x 10^3 x 0.987 atm = 59.220 atm

(b) diamond

(c) $dT/dP = T(V^l - V^g)/\Delta H = 0$ at 70 kilobars and 4700 K

2.8.2.6. On the basis of the following data for the vapor pressure of solid palladium metal as a function of temperature evaluate $\Delta^{sub}H°$ - the mean enthalpy of sublimation of palladium in kcal $mole^{-1}$.

T(K)	P(torr)x10^{-4} (1 torr = 1mm Hg)
1294	2.17
1308	3.19
1322	5.23
1333	6.01
1350	8.22
1396	24.5
1406	29.0
1426	47.8
1459	88.6
1488	168.0

Solution

Plot lg P vs 1/T (like in figure). Slope = -ΔH/2.303R.

$$\text{Slope} = \frac{\Delta(\lg P)}{\Delta(1/T)} = \frac{(1.800 - 0.400)}{(6.90 - 7.22)\times 10^{-4}} = -1.95\times 10^4 \text{ K}$$

$\Delta^{sub}H°$ = -2.303 R x Slope

= 2.303 x 1.987 x 1.95 x 10^4

= 89200 cal $mole^{-1}$ or 89.2 kcal $mole^{-1}$

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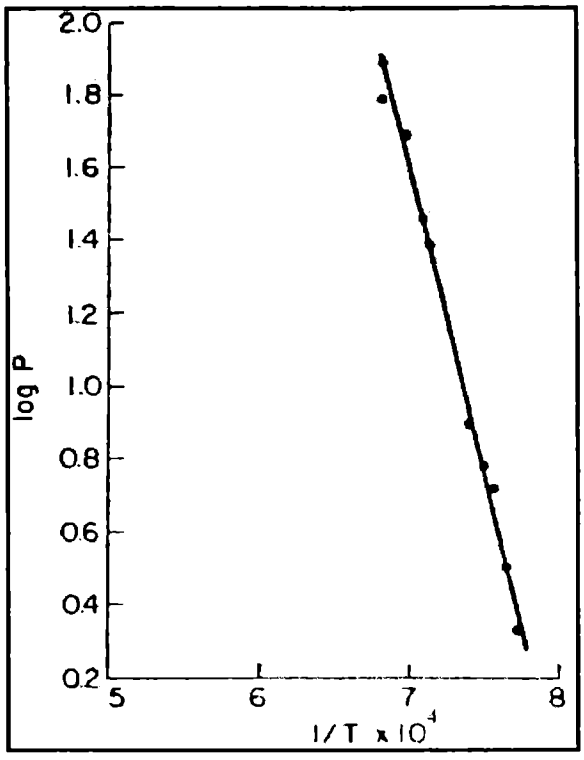

2.8.2.7. For a certain compound Y, the vapor pressure of the solid and the vapor pressure of the liquid are given as follows:

Vapor pressure of solid Y	Vapor pressure of liquid Y
200K 25 mm Hg	300K 150 mm Hg
250K 75 mm Hg	400K 300 mm Hg

Calculate (a) the enthalpy of sublimation, (b)the enthalpy of vaporization, (c)the enthalpy of fusion. All calculations are to be in cal mole^{-1}.

Solution

(a) Y(s) ⇆ Y(g)

$$\Delta^s H : \lg\frac{P_2}{P_1} = \frac{\Delta^s H(T_2 - T_1)}{2.303RT_1T_2}$$

$$\Delta^s H = \frac{\lg(75/25)\times 2.303\times(200\times 250)\times 1.987}{50} = 2183 \text{ cal mole}^{-1}$$

$$\text{(b) } \Delta^v H: \lg\frac{P_2}{P_1} = \frac{\Delta^v H(T_4 - T_3)}{2.303RT_4T_3}$$

$$\Delta^v H = \frac{\lg(300/150)\times 2.303\times(300\times 400)\times 1.987}{100} = 1653 \text{ cal mole}^{-1}.$$

(c) $\Delta^f H : \Delta^{sub} H = \Delta^f H + \Delta^v H$; $\Delta^f H = \Delta^{sub} H - \Delta^v H = 530$ cal mole^{-1}

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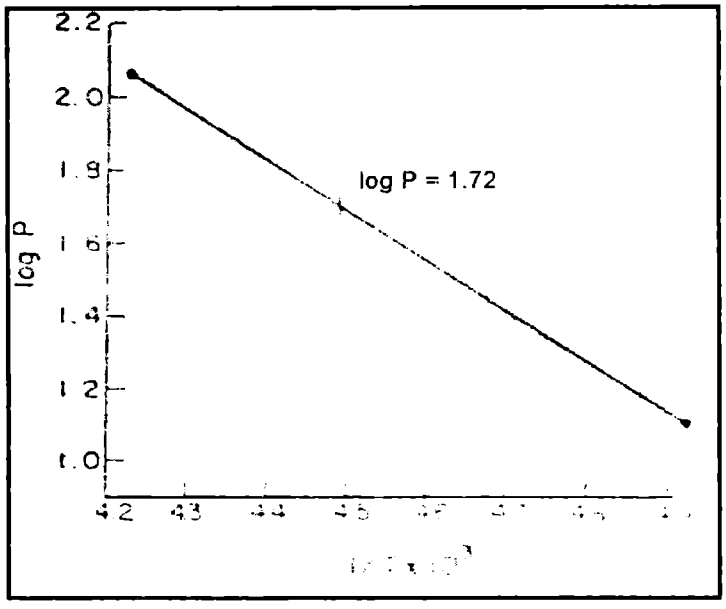
2.8.2.8. The vapor pressure of methyl bromide is 13.0 mm Hg at –70.0°C and 117 mm Hg at –36.7 °C. Evaluate (a) the molar enthalpy of vaporization of methyl bromide, (b) the vapor pressure of methyl bromide at –50.0 °C.

Solution

(a) Plot log P vs 1/T. (See figure). Slope = - $\Delta^{v}H/2.303\ R$

$$\text{Slope} = \frac{\Delta(\lg P)}{\Delta(1/T)} = \frac{2.068-1.114}{0.004228-0.004921} = -1378$$

$\Delta^{v}H = 2.303 \times 1.987 \times 1378 = 6306$ cal mole $^{-1}$



(b) At -50°C, T = 223.2°K, 1/T = 0.00448 K^{-1}. From graph, lg P = 1.72 at 1/T = 0.00448

P =52 mm Hg.

2.8.2.9. The following data were obtained for the vapor pressures of liquid and solid $SnBr_4$ at various temperatures:

	Solid		Liquid	
t(°C)	9.8	21.0	30.7	41.4
P (mm Hg)	0.116	0.321	0.764	1.493

Calculate (a) the triple point, (b) the molar enthalpy of sublimation, and (c) the molar enthalpy of fusion, of $SnBr_4$. Solve (b) and (c) both by an algebraic method and by a graphical method.

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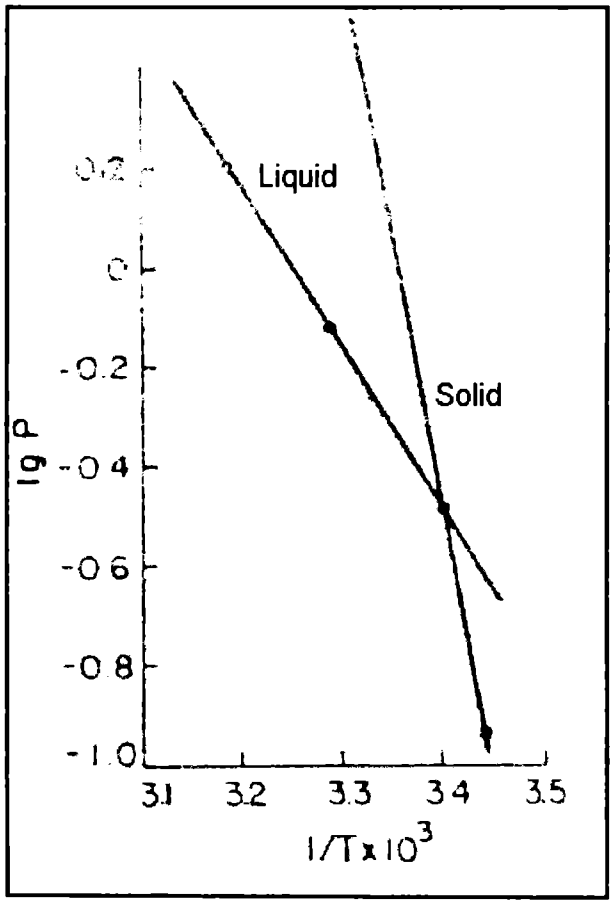
Solution

(a) plot lg P vs. 1/T for the solid and lgP vs. 1/T for the liquid on the same graph. The point of intersection gives lg P and 1/T for the triple point.

	Solid		Liquid	
t(°C)	9.8	21.0	30.7	41.4
T(K)	283.0	294.2	303.9	314.6
1/T	0.003534	0.003399	0.003291	0.003179
P (mm Hg)	0.116	0.321	0.764	1.493
lgP	-0.9355	– 0.4935	-0.1169	+0.1741



It is better to plot lgP vs. 1/T instead P vs T because lg P vs. 1/T is a straight line function and can be extrapolated whereas the P vs T is curved.

The intersection is at $(1/T)\cdot 10^3 = 3.4$; $T = \dfrac{10^3}{3.4} = 294K$

(b) Algebric method.

From the integrated form of Clausius-Clapeyron equation

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$$\lg\frac{P_2}{P_1} = -\frac{\Delta^{sub}H}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\lg\frac{0.321}{0.116} = -\frac{\Delta^{sub}H}{2.303\times1.987\times10^{-3}}\left(\frac{1}{294.2} - \frac{1}{283.0}\right) = 15.04 \text{ Kcal}$$

Graphical method

The indefinite integral of the Clausius-Clapeyron equation is:

$$\lg P = -\frac{\Delta H}{2.303R}\times\frac{1}{T} + const.$$

A plot of lg P vs.1/T should give a straight line with a slope of -ΔH/R.Thus the slope of sublimation line is - Δ^{sub}H/4.585 .The slope can be determine graphically and Δ^{sub} H can be calculated.

(c) $$\lg\frac{P_4}{P_3} = -\frac{\Delta^{v}H}{2.303R}\left(\frac{1}{T_4} - \frac{1}{T_3}\right)$$

$$\lg\frac{1.493}{0.764} = -\frac{\Delta^{v}H}{2.303\times1.987\times10^{-3}}\left(\frac{1}{314.6} - \frac{1}{303.9}\right) \qquad \Delta^{v}H = 11.89 \text{ Kcal}$$

$\Delta^{f}H = \Delta^{sub}H - \Delta^{v}H = 15.04 - 11.89 = 3.14$ kcal mole^{-1}

2.8.2.10. For liquid thiacyclobutane the vapor pressure (in mm Hg) can be expressed by the equation:

$$\lg P = 7.01667 - \frac{1321.331}{t + 224.513}$$

with t in °C. Calculate $\Delta^{v}H$ at 298K.

Solution

The indefinite integral of the Clausius-Clapeyron equation is:

$$\lg P = -\frac{\Delta^{v}H}{2.303R}\cdot\frac{1}{T} + const$$

We compare the two equations and

$$-\frac{1321.331}{25 + 224.513} = -\frac{\Delta^{v}H}{2.303\times1.987\times293}$$

$\Delta^{v}H = 7100$ cal = 7,1Kcalmole^{-1}

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2.8.2.11. The vapor pressure of liquid helium can be expresses by the equation:

$$P = AT^{5/2} \cdot e^{-[(a/T)+bT^{5.5}]}$$

In which A, a, b are constants. Derive an equation for $\Delta^v H$ as a temperature function.

Solution

$$\ln P = \ln A + \frac{5}{2}\ln T - \frac{a}{T} - bT^{5.5}$$

In the same time the indefinite integral of the Clausius-Clapeyron is:

$$\ln P = - \frac{\Delta^v H}{RT} + ct$$

If we compare these two equation we get

$$-\frac{\Delta^v H}{RT} = \frac{5}{2}\ln T - \frac{a}{T} - bT^{5.5}$$

and

$$\Delta^v H = Ra - \frac{5RT}{2}\ln T + bRT^{6.5}$$

2.8.2.12. (a) Estimate $\Delta P/\Delta T$ in triple point of water (T=273.16K and P=4.585 mmHg) for the equilibrium H_2O (s) $\leftrightarrows$ H_2O (l) if $\rho^{s}_{H_2O}$ = 0.9168 kg l^{-1}, $\rho^{l}_{H_2O}$ = 0.9998 kg l^{-1} and $\Delta^f S$ = 22j $mole^{-1}$ K^{-1}.

(b) Estimate the effect of atmospheric pressure on crystallizing point.

Solution

$$\text{(a) } V^{s}_{H_2O} = \frac{18g \cdot mole^{-1} \cdot 10^{-3} Kg \cdot g^{-1}}{0.9168 Kg \cdot l^{-1}} = 19.634 \cdot 10^{-3} \text{l mole}^{-1}$$

$$V^{l}_{H_2O} = \frac{18g \cdot mole^{-1} \cdot 10^{-3} Kg \cdot g^{-1}}{0.9998 Kg \cdot l^{-1}} = 18.004 \cdot 10^{-3} \text{l mole}^{-1}$$

$$\left(\frac{\Delta P}{\Delta t}\right)_{sl} = \frac{22 j \cdot mole^{-1} K^{-1}}{(18.004 - 19.634)10^{-3} l \cdot mole^{-1}}$$

$$= -13.496 \cdot 10^{3} \text{ J l}^{-1} \cdot \frac{0.082 l \cdot atm \cdot mole^{-1} K^{-1}}{8.314 j \cdot mole^{-1} \cdot K^{-1}} = -133.12 \text{ atm K}^{-1}$$

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$$\text{(b) } \Delta T = \frac{\Delta P}{(-133.12 atm \cdot K^{-1})} = \frac{(760 - 4.585) mmHg \dfrac{1 atm}{760 mmHg}}{-133.12 atm \cdot K^{-1}}$$

$$= -0.00747 \text{ K} \approx -0.01 \text{ K}$$

2.8.2.13. Calculate $\Delta P/\Delta T$ in triple point of water for the equilibrium H_2O (l) ⇆ H_2O (v) if $\Delta^v H$ = 44.998 j mole^{-1}, the pressure of triple point is 4.585 mm Hg and V'_{H_2O} = 18.004·10^{-3} l mole^{-1}.

Solution

$$V^v_{H_2O} = 22.414 \text{ l mole}^{-1} \frac{760 mmHg}{4.585 mmHg} = 3.715 \text{ x } 10^3 \text{ l mole}^{-1}$$

$$\frac{\Delta P}{\Delta T} = \frac{\Delta^v H}{T \Delta V} = \frac{44.998 j \cdot mole^{-1}}{(273.16 K)(3715 - 18 \cdot 10^{-3}) l \cdot mole^{-1}} \frac{0.082 l \cdot atm \cdot mole^{-1} \cdot K^{-1}}{8.314 j \cdot mole^{-1} \cdot K^{-1}}$$

$$= 4.373 \ 10^{-4} \text{ atm K}^{-1}$$

2.8.2.14. Estimate $\Delta P/\Delta T$ for sublimation effect in triple point of water if $\Delta^{sub}H$ = 50,999 j mole^{-1}, $V^s_{H_2O}$ =19.634 10^{-3} l mole^{-1}, $V^v_{H_2O}$ =3.715 x 10^3 l mole^{-1}.

Solution

H_2O (s) ⇆ H_2O (v)

$$\frac{\Delta P}{\Delta T} = \frac{50999 J mole^{-1}}{273.16 K (3715 - 19634 \cdot 10^{-3}) l mole^{-1}} \cdot \frac{0.082 l \cdot atm \cdot mole^{-1} \cdot K^{-1}}{8.314 j \cdot mole^{-1} \cdot K^{-1}}$$

$$= 4.956 \cdot 10^{-4} \text{ atm K}^{-1}.$$

2.8.2.15. Derive an equation for the temperature dependence of the vapor pressure of a liquid (analogus to the integrated Clausius-Clapeyron equation) assuming that the vapor has the equation PV = RT + K where K is a constant.

Solution

$$\frac{dP}{dT} = \frac{\Delta^v H}{T(V^v - V')} \approx \frac{\Delta^v H}{TV^v} = \frac{\Delta^v H \cdot P}{T(RT + K)}$$

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$$\frac{dP}{P} = \frac{\Delta^v H dT}{T(RT + K)}$$

$$\frac{1}{T(RT + K)} = \frac{A}{KT} + \frac{B}{K(RT + K)}$$

$K^2 = KA(RT + K) + BKT = AK^2 + KT(B + AR)$

$A = 1; B + AR = 0\ B = - R$

Then

$$\frac{1}{T(RT + K)} = \frac{1}{KT} + \frac{R}{K(RT + K)} \quad ; \qquad \frac{dP}{P} = \frac{\Delta^v H dT}{KT} - \frac{R\Delta^v H dT}{K(RT + K)} \text{ and}$$

$$\ln\frac{P_2}{P_1} = \frac{\Delta^v H dT}{K}\ln\frac{T_2}{T_1} - \frac{\Delta^v H}{K}\ln\frac{RT_2 + K}{RT_1 + K} = \frac{\Delta^v H}{K}\ln\frac{T_2(RT_1 + K)}{T_1(RT_2 + K)}$$

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2.8.3. TWO COMPONENT SYSTEMS

2.8.3.1. ISOTHERMAL EQUILIBRIUM. RAOULT'S AND HENRY'S LAW

2.8.3.1.1. Explain why, even in a nonideal solution, the vapor pressure of the solvent is given by Raoult's law when the solution is dilute.

Solution

In a dilute solution a solvent molecule has only other solvent molecules around. The energy necessary to escape from the surface is practically the same like in pure solvent. The vapor pressure of the solvent in solution is less then in pure solvent, not because each molecule is held more firmly in solution but because there are fewer solvent molecules. The number of solvent molecule is less in the ratio χ_1, and the vapor pressure is less in the same ratio: $P_1 / P_1^0 = \chi_1$, which is Roult's law.

2.8.3.1.2. When 1.046 g of cadmium is dissolved in 25.23 g of mercury the vapor pressure of resulting amalgam at 32.2^{0}C is 0.92 times that of pure mercury. What are:
(a) activity and (b) the activity coefficient

Solution

(a) $a_1 = \dfrac{P_1}{P_1^0} = 0.92$

(b) $\gamma_1 = \dfrac{a_1}{\chi_1} = \dfrac{0.92}{\dfrac{25.23/200.61}{(25.23/200.61+1.046/112.41)}} = 0.989$

2.8.3.1.3. Let us consider the distillation of myristic acid ($C_{13}H_{27}COOH$) with steam. At 200^{0}C, the saturated vapor pressure of myristic acid is 14.5 mmHg. By passing superheated steam at 200^{0}C and 740 mmHg over the acid, we get a mixture of vapors at the same pressure and temperature. Calculate the amount of water (superheated stem at 200^{0}C) for the distillation of 1 kg of acid.

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Solution

The mole fractions (1-y) of the steam and y of the acid will be calculate from equation $P_1^0 = (1-y)\cdot P$ and $P_2^0 = y \cdot P$

$$1-y = \frac{740-14.5}{740} = 0.98 \text{ and } y = \frac{14.5}{740} = 0.02$$

The following mass quantities of the components (per mole of vapor mixture) are obtained in the condensate:

water.....$m_1 = (1-y)\cdot M_1 = 0.980 \text{ x } 18 = 16.64$ g

acid.....$m_2 = y \cdot M_2 = 0.02 \text{ x } 228 = 4.56$

For the distillation of 1 kg of acid is necessary to distill 16.64 : 4.56 = 3.65 kg of water.

2.8.3.1.4. A and B from an ideal solution. The vapor pressure of pure A at 25^0C is 100 mmHg. The vapor pressure of B is zero. The vapor pressure at 25^0C of a solution consisting of 1 g B and 10 g A is 95 mmHg.

Calculate the ratio of the molecular weight of B to the molecular weight of A.

Solution

$$\chi_B = \frac{P_A^0 - P_A}{P_A^0} \text{ and } P_A^0 - P_A = P_A^0 \chi_B$$

$$100-95 = \chi_B \times 100,\ \chi_b = 0.05$$

$$\chi_B = \frac{m_B / M_B}{m_A / M_A + m_B / M_B} = \frac{1}{1+\frac{m_A / M_A}{m_B / M_B}}$$

$$\frac{m_A M_B}{m_B M_A} = \frac{1}{\chi_B} - 1 = 19;\ \frac{M_B}{M_A} = 19\frac{m_B}{m_A} = 1.90$$

2.8.3.1.5. At a given temperature, the vapor pressure of pure C and pure D are 550 and 250 mmHg, respectively. By a graphical construction, estimate

(a) the total vapor pressure above a solution that contains 25 mole percent of D;

(b) the partial pressure of D in the mixture;

(c) the composition of a solution with a vapor pressure of 500 mmHg.

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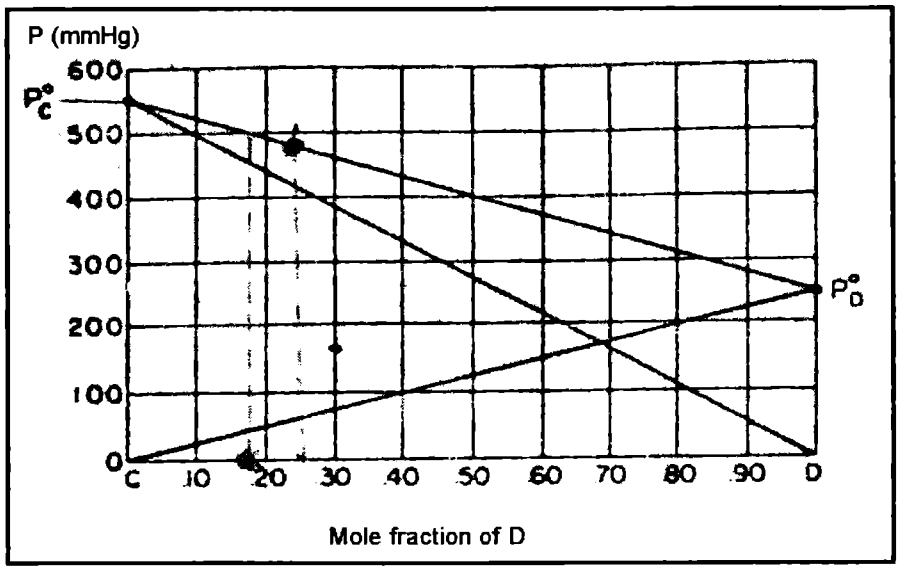
Solution



From the graph:

(a) 475 mmHg

(b) 62.5 mmHg, because 475 = P_D + 0.75 x 550

(c) 17 percent D

2.8.3.1.6. In order to find out whether the formula of sodium – tellurium complex in liquid ammonia is $NaTe_x$ or Na_2Te_x in the table are presented the vapor pressure of a series of solutions prepared by dissolving m = 0.1398 g of sodium, at 20^0C, in liquid ammonia in presence of an excess of solid tellurium. The vapor pressure of pure liquid NH_3 at 20^0C is 6428 mmHg.

$m_{NH_3(l)}(g)$	$\chi_{Na} \times 10^4$	ΔP (mmHg)
38.909	26.5	8.2
28.767	35.9	12.0
20.904	49.3	17.0
15.272	67.3	22.8
11.362	90.6	32.0

On the basis of these data, make a decision which of the two formulas for sodium – tellurium complex is correct one.

Solution

According to Raoult's law

$$P^0_{NH_3(l)} - P_{NH_3(l)} = \chi_{Na} \cdot P_{NH_3(l)}, \ \Delta P = \chi_{Na} \cdot P^0_{NH_3(l)}$$

$$\frac{\Delta P}{\chi_{Na} \cdot P^0_{NH_3(l)}} = 0.48;\ 0.52;\ 0.54;\ 0.53;\ 0.55$$

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Assuming that the dissolved compound does not dissociate, the number of moles of compound formed per mole of Na used is equal (relative vapor pressure depression) divided by the mole fraction of Na) ≅ 0.5.

In other words there are two Na atoms per molecule of compound, so correct formula is Na_2Te.

2.8.3.1.7. The following table gives the vapor pressures of water and acetone in equilibrium with their solutions of the compositions given, at 25^0C.

Mole fraction of acetone in liquid	Partial vapor pressure, (mmHg)	
	Acetone	Water
0	0	24
0.0333	38	23
0.117	105	23
0.236	146	22
0.420	164	22
0.737	192	17
1.00	229	0

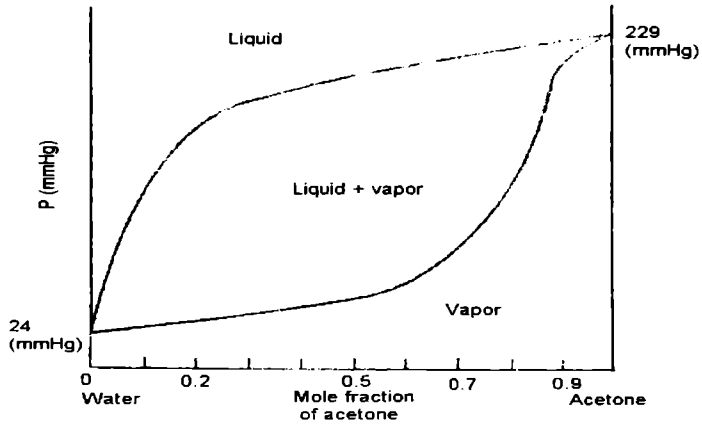
(a) Plot a phase diagram showing the total vapor pressure of water-acetone solutions as functions of the mole fractions of acetone in the liquid and in the vapor. Label each region in your diagram to show the phases present when the pressure and gross composition of system are represented by a point in that region.

(b) Calculate (as nearly as you can from the data given) the Henry's law constant for acetone in the solvent water.

(c) Find the activity coefficient of acetone in the solution in which its mole fraction is 0.420 (i) taking pure acetone as the standard state; (ii) treating acetone as the solute, so that the activity coefficient as acetone becomes 1.00 in the limit of pure water. Use the mole fraction as the measure of composition in both cases.

Solution

(a) See figure.



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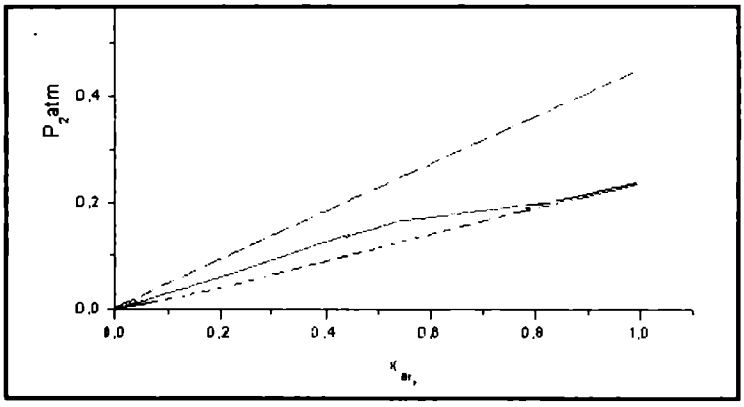
(b) $k_A = P_A / \chi_A$. We take the values given for the most dilute solution:

(c) (i) $\gamma_A = \dfrac{P_A}{\chi_A P_A^0} = \dfrac{164}{0.420 \times 229} = 1.71$

(ii) $\gamma_A = \dfrac{P_A}{\chi_A k_A} = \dfrac{164}{0.420 \times 1140} = 0.343$

2.8.3.1.8. Figure shows the partial vapor pressure of bromine over its solutions in carbon tetrachloride at 25^0C. These solutions show a positive deviation from Raoult's law. The vapor pressure of pure bromide $P_2^0 = 0.280$ atm at 25^0 and the ratio $p_2^\infty / \chi_2^\infty$ in the region of dilute solutions ($\chi_2 \cong 0.004 - 0.025$) is equal to 0.539 atm (the value of Henry's coefficient for solutions of Br_2 in CCl_4).

Calculate activities and activity coefficients of bromine in its solutions in CCl_4, selecting the standard state (a) when the bromide is solvent and (b) when the bromide is solute at $x_2 = 0.4$ and $P_2 = 0.146$ atm.



Solution

(a) $\gamma_i = \dfrac{a_i}{\chi_i} = \dfrac{f_i}{f_i^0 \chi_i} = \dfrac{P_i}{P_i^0 \chi_i}$

We have positive deviations when $\gamma_i > 1$, since $P_i > P_i^0 \chi_i$; and negative deviations when $\gamma_i < 1$ since $P_i < P_i^0 \chi_i$. In infinity dilute solutions which Raoult's law can be applied to, the activity coefficient of solvent is equal to unity

$$P_1^\infty = P_1^0 \cdot \chi_1^\infty \text{ and } y_1^\infty = \frac{a_1^\infty}{\chi_1^\infty} = \frac{P_1^\infty}{P_1^0 \cdot \chi_1^\infty} = 1$$

(the superscript ∞ denotes infinite dilution).

In our case, considering the vapor to be an ideal gas, we get the standard fugacity of

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bromine according to this method $f_2^0 = 0.280$.

$$a_2 = \frac{P_2}{P_2^0} = \frac{0.146}{0.280} = 0.521$$

$$\gamma_2 = \frac{a_2}{\chi_2} = \frac{0.521}{0.4} = 1.30$$

(b) for a solution whose vapor is an ideal gas, and the standard state of the component is not the pure liquid component, but some other state.

$$a_2 = \frac{P_2}{f_2^0} \text{ and } f_2^0 = \frac{P_2}{a_2} = \frac{P_2^\infty}{a_2^\infty} = \frac{P_2^\infty}{\chi_2^\infty}$$

We get $a_2' = \frac{P_2}{f_2^0} = \frac{P_2}{P_2^\infty / \chi_2^\infty} = \frac{0.146}{0.539} = 0.27$

$$\gamma_2' = \frac{a_2'}{\chi_2} = \frac{0.27}{0.4} = 0.675$$

2.8.3.1.9. Given the following vapor pressure of chloroform (C), $CHCl_3$, and acetone (A), $(CH_3)_2CO$, over a solution of these components, at 35.17^0C:

Mole fraction, χ_C	P_C, (mmHg)	P_A, (mmHg)
0	0	344.5
0.0588	9.2	323.2
0.1232	20.4	299.3
0.1853	31.9	275.4
0.2970	55.4	230.3
0.5143	117.8	135.0
0.7997	224.4	37.5
0.9175	267.1	13.0
1.0000	291.1	0

(a) Find the activity coefficients (γ) of C and of a on the mole fraction scale, referred to the pure substances as the standard states, in a solution 51.43 mole percent C.

(b) Find the Henry's law constant k (where P = kx) for each of the components in orther as nearly as you can without elaborate analysis of the data.

(c) Find the activity coefficient (γ'_C) of C on the mole fraction scale, referred to the infinitely dilute solution of C in A, in a solution 51,43 mole percent C. ($\gamma'_C \to 1$ as $X_C \to 0$).

(d) Calculate the ratio γ' / γ for each of the components. Is the result dependent on the mole fraction?

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(e) Find ΔG for the process of mixing 0.5143 mole C and 0.4857 mole A at 35.17^{0}C.

Solution

(a) $\gamma_C = \frac{P_C}{\chi_C P_C^{\infty}} = \frac{117.8}{0.5143 \times 293.1} = 0.782$; $\gamma_A = \frac{P_C}{\chi_A P_A^0} = \frac{135.0}{0.4857 \times 344.5} = 0.807$

(b) $k_C = \frac{P_C}{\chi_C} = \frac{9.2 mmHg}{0.0588} = 156 mmHg$

We use P_C and χ_C for the most dilute solution for which data are given.

$k_A = \frac{P_A}{\chi_A} = \frac{13.0 mmHg}{0.0825} = 158 mmHg$

(c) $\gamma_C' = \frac{P_C}{k_C \chi_C} = \frac{117.8}{156 \times 0.5143} = 1.468$

(d) $\frac{\gamma_C'}{\gamma_C} = \frac{P_C}{k_C \chi_C} \cdot \frac{P_C^0 \chi_C}{P_C} = \frac{P_C^0}{k_C} = \frac{293.1}{156} = 1.88$

$\frac{\gamma_A'}{\gamma_A} = \frac{P_A^0}{k_A} = \frac{344.5}{158} = 2.18$

These rations are independent of the composition of the solution.

(e) $\Delta G = 0.5143\mu_C + 0.4857\mu_A - (0.5143\mu_C^0 + 0.4857\mu_A^0)$

$= 0.5143(\mu_C - \mu_C^0) + 0.4857(\mu_A - \mu_A^0) = 0.5143RT \ln a_C + 0.4857RT \ln a_A$

$= RT[0.5143 \ln(\gamma_C \chi_C) + 0.4857 \ln(\gamma_A \chi_A)]$

$= 2.303RT[0.5143 \lg(0.782 \times 0.5143) + 0.4857 \lg(0.802 \times 0.4857)]$

$= 2.303 \times 1.987 \times 308.32 \times (-0.4026) = -568$ cal

2.8.3.1.10. Vapor pressure of water-ethanol solutions at 20^{0}C are:

Weight percent ethanol	0	20	50	80	100
P_{H_2O} (mmHg)	17.5	15.9	14.5	11.3	0
$P_{C_2H_5OH}$ (mmHg)	0	12.6	23.5	31.2	43. 6

For the reaction C_2H_4 (g) + H_2O (l) ⇆ C_2H_5OH (l)

K = 10.0 at 25^{0}C. Find the pressure of C_2H_4 in equilibrium with a solution containing equal weights of H_2O and C_2H_5OH at 25^{0}C (a) assuming that the solution is ideal, (b) using the best information available to you.

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Solution

$$\frac{a_{C_2H_5OH}}{P_{C_2H_4}a_{H_2O}} = K = 10.0$$ where a represents activity

$$P_{C_2H_4} = \frac{a_{C_2H_5OH}}{10.0a_{H_2O}}$$

(a) In an ideal solution the activity is equal to the mole fraction

$$a_{C_2H_5OH} = \chi_{C_2H_5OH} = \frac{1/46.07}{1/46.07 + 1/18.2} = 0.281,$$ where 46.07 and 18.02 are the molecular weights of C_2H_5OH and H_2O, respectively.

$$a_{H_2O} = 0.719$$

$$P_{C_2H_4} = \frac{0.281}{10.0 \times 0.719} = 0.0392 \text{ atm}$$

(b) For each component $a = P/P^o$, where P is the vapor pressure of the component in solution and P^o is the vapor pressure of the pure component.

$$a_{C_2H_5OH} = \frac{23.5}{43.6} = 0.539;\ a_{H_2O} = \frac{14.5}{17.5} = 0.828$$

$$P_{C_2H_4} = \frac{0.539}{10.0 \times 0.828} = 0.0651 \text{ atm}$$

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2.8.3.2. ISOBARIC EQUILIBRIUM. EBULIOSCOPY AND CRYOSCOPY

2.8.3.2.1. An aqueous solution contains 5 gr of a substance, which molecular weight is 140g mole^{-1}, in 250 g of water. Estimate the boiling point elevation of water if $\Delta^v H_2O = 40{,}660$ Kj mole^{-1}.

Solution

(a) $n_1 = \dfrac{250g}{18g \cdot mole^{-1}} = 13.889$ mole

$n_2 = \dfrac{5g}{140g \cdot mole^{-1}} = 0.036$ mole

$x_1 = \dfrac{13.889}{13.889 + 0.036} = 0.9974$

$\ln x_1 = -\dfrac{\Delta^v H_{H_2O}}{R} \cdot \dfrac{\Delta T_b}{T_b^2}$

$$\Delta T_b = -\frac{RT_b^2 \cdot \ln x_1}{\Delta^v H_{H_2O}} = -\frac{(8.314 j \cdot mole^{-1} \cdot K^{-1})(373K)^2}{40660 j \cdot mole^{-1}} \ln 0.9974 = 0.0741 \text{ K.}$$

(b) The value of ΔT_b can be obtained from equation

$\Delta T_b = 0.513m$, where 0.513 K mole^{-1} is ebullioscopic constant of water.

$m = \dfrac{5g}{140g \cdot mole^{-1}} \cdot \dfrac{1000g}{250g} = 0.143$ mole

$\Delta T_b = (0.513 \text{ K mole}^{-1})(0.143 \text{ mole}) = 0.0734$ K.

2.8.3.2.2. The boiling temperature of acetic acid is 118.0°C. A solution that contains 0.3027 g antracene and 28.95 acetic acid boils at 184°C.

The molal boiling-point elevation (K_e) of the acetic acid is 3.1. Estimate molecular weight of antracene.

Solution

$$M_2 = \frac{1000 K_e \cdot m_2}{m_1 \cdot \Delta T} = \frac{1000 \times 3.1 \times 0.3027}{28.95 \times 0.184} = 176 \text{ g mole}^{-1}$$

The calculated molecular weight is $C_{14}H_{10}$ =14 x 12 + 10 = 168 + 10 = 178 g mole^{-1}

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2.8.3.2.3. The cryoscopic constant for benzene is 5.085°C (K. kg. mole^{-1}). A 0.07734 molal solution of tetraisoamyl-ammonium thiocyanate in benzene had a freezing point of 0.01573°C lower than that of pure benzene. calculate the association number of the quaternary ammonium salt that is the ratio of the apparent molecular weight to the formula weight, in benzene.

Solution

$$m = \frac{\Delta T}{K_f} = \frac{0.01573}{5.085} = 0.00309$$

$$\text{Associated number} = \frac{\textit{molality based on formula weight}}{\textit{observed molality}} = \frac{0.07734}{0.00309} = 25$$

2.8.3.2.4. The freezing point depression constant for camphor is 40.27°C (kg camphor) (mole solute)$^{-1}$. In an experiment 0.0113 g of phenanthrene lowered the freezing point of 0.0961 g of camphor by 27°C. What is the molecular weight of phenanthrene in camphor?

Solution

The freezing point lowering for dilute solution depends only on the properties of pure solvent and it is

$$\Delta T = K_f \cdot \frac{1000 m_2}{m_1 M_2}$$

where m_1 and m_2 are mass amounts of components K_f is crioscopic constant and M_2 - molecular weight of solute.

$$M_2 = K_f \cdot \frac{1000 m_2}{\Delta T m_1} = 40.27 \cdot \frac{1000 \times 0.0113}{0.0961 \times 27} = 177.$$

The value calculated from atomic weights is 178.

2.8.3.2.5. The formula for the relationship between the solute concentration and freezing point depression of solution is assumed that the enthalpy of fusion of the solvent does not vary with temperature.

In the case of water this is not a good assumption as the enthalpy of fusion of ice changes at the rate of 1.6 percent per degree in the vicinity of 0°C. Derive a formula

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for the molar fraction of solute in solution, x_2, as a function of freezing point, using the equation $\Delta^f H_{ice} = -6997 + 63.68\ T - 0.1586\ T^3$ cal mole^{-1}.

Solution

$$\frac{\partial \ln P}{\partial T} = \frac{\Delta H}{RT^2}\ ;\ d\ln P = \frac{\Delta^f H}{RT^2}dT$$

$$d\ln P = \frac{\Delta^f H}{RT^2}dT = \frac{1}{RT^2}\left[-6997 + 63.68T - 0.1586T^3\right]dT =$$

$$= \left[-\frac{6997}{R}\cdot\frac{1}{T^2} + \frac{63.68}{R}\cdot\frac{1}{T} - \frac{0.1586}{R}\cdot T\right]dT$$

$$\ln\frac{P}{P^0} = \frac{6997}{R}\left[\frac{1}{T} - \frac{1}{T^0}\right] + \frac{63.68}{R}\ln\frac{T}{T^0} - \frac{0.1586}{R}(T - T^0)$$

$$\ln(1 - x_2) = 3521\ \frac{T^0 - T}{T^0 T} + 73.8\lg\frac{T}{T^0} - 0.0798(T - T^0)$$

$$x_2 \approx 3521\ \frac{T^0 - T}{T^0 T} - 73.8\lg\frac{T}{T^0} + 0.0798(T - T^0)$$

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2.8.3.3. PARTITION COEFFICIENT OF A SUBSTANCE IN TWO IMMISCIBLE SOLVENTS

2.8.3.3.1. Compute the activity coefficient of mercury chloride in its aqueous solution at 0.2866, using the following experimental date on the distribution of mercury chloride between water and benzene:

C_{H_2O} (mole l^{-1})	0.001845	0.00369	0.00728	0.0648	0.01578	0.2866
$C_{C_6H_6}$ (mole l^{-1})	0.000155	0.00031	0.000618	0.00924	0.01222	0.0210
$K_{Nernst} = \frac{C_{H_2O}}{C_{C_6H_6}}$	11.90	11.90	11.90	12.35	12.90	13.61

Solution

These data show that at low concentrations of $HgCl_2$ in solutions K_{Nernst} = 11.9; consequently, the ratio of the activities of $HgCl_2$ in both liquid phases at any concentration will be 11.9.

$$a_{H_2O} = 11.9 \cdot a_{C_6H_6} = 11.9 \times 0.021 = 0.25$$

$$f_{H_2O} = \frac{a_{H_2O}}{C_{H_2O}} = \frac{0.25}{0.2866} = 0.872$$

2.8.3.3.2. Assume that we have a dm^3 of an aqueous solution and b dm^3 of the ether and that the solutions of the substance to be extracted in both solvents are so dilute that the partition coefficient is expressed by equation $K_{part} = \frac{C_{ether}}{C_{water}}$.

Calculate how much will be the residue in water if (a) the initial solution contains m "grammes of the substrate and a = 1 dm^3, b = 1 dm^3 and K_{part} = 2 after a single extraction; (b) upon ten-fold extractions.

Solution

(a) if the initial aqueous solution contained m grammes of substance, then after extraction with b dm^3 of the ether mx grammes of the substance will remain in the aqueous solution (x is the fraction of the substance remaining in the solution), and m(1-x) grammes will pass over into the ether layer. So we get

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$$K_{part} = \frac{m(1-x)}{b} : \frac{mx}{a} \quad \text{whence} \quad x = \frac{a}{a + bK_{part}}$$

After each repeated extraction of the substance with b dm^3 of ether from the same a dm^3 of the aqueous solution, there will remain in the latter fraction x of the amount present before extraction.

As a result of n repeated extractions using identical volumes of ether a fraction of the substance equal to x^n will remain in the water.

(b) After a single extraction, using the entire available amount of extracting liquid at once, the residue in the water will be $mx = m\frac{1}{1+2} = 0.33m$.

Upon ten-fold extraction using 0.1 dm^3 portions of the ether, the residue in water will be

$$mx^n = \left(\frac{1}{1+0.1\times 2}\right)^{10} = 0.16m$$

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REFERENCES

1. F. T. Wall, "Chemical Thermodynamics", A course of study – the third edition, W. H. Freeman and Company, San Francisco, 1974.
2. M. H. Everdell, "Intrduction to Chemical Thermodynamics", Edition Revolucionaria, Instituto Cubano del Libro, 1965.
3. M. Kh. Karapetyants, "Chemical Thermodynamics", MIR Publishers, 1978.
4. R. J. Bearman, B. Chu, "Problems in Chemical Thermodinamics", Addison-Wesley Publishing Company, 1967.
5. Z. Cenuse, "Introduction in Chemical Thermodynamics", University Press Co., Bucharest, 2004.
6. D.R. Stull and G.C. Sinke, "Thermodynamic Properties of the Elements", American Chemical Society, Washington DC, 1956.
7. "The NBS Tables of Chemical Thermodynamic Properties" J. Phys. Chem. Ref. Data 11, Supplement No. 2, 1982.
8. Handbook of Chemical Property Estimation Method, McGrow – Thill, NY, 1993.
9. I. M. Klotz and R. M. Rosenbeng, "Chemical Thermodinamics. Basic Theory and Methods, John Wiley and Sons, N.Y., 1994.
10. S.E. Wood an R. Battino, "Thermodynamic of Chemical Systems", Cambridge University Press, Cambridge, 1990.
11. D. R. Lide, "Handbook of Chemistry and Physics", CRC Press, Boca Raton, Boston, 1998 – 1999.
12. L. C. Labobitz and J. S. Arents, "Physical Chemistry" John Willey and Sons, N. Y., 1993.
13. S. I. Sandler, "Models for Thermodynamic and Phase Equilibria Calculations", Marcel Dekker Inc., N.Y., 1994.
14. M. H. Everdell, "Introduction to chemical thermodynamics", Edition Revolucionaria, Instituto Cubano del Libro, 1965.
15. M. Kh. Karapetyants, "Chemical thermodynamics", MIR Publishers, 1978.
16. R. J. Bearman, B. Chu, "Problems in chemical thermodynamics", Addison-Wesley Publishing Company, 1967.
17. B. W. Rossiter and R. C. Baetzold, "Physical Methods of Chemistry", Vol. 6, John Wiley and sons, New York, 1992.

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APPENDIX

TABLE 1. Basic Thermodynamic Properties of Selected Chemical Compounds in Standard Conditions (25 ^{0}C and 1 atm)

$\Delta H^0_{298} = Q_p$ = heat of formation of a mole of the compound from elements in the standard state, (kcal/mol)

ΔG^0_{298} = change in Gibbs energy, (kcal/mol)

S^0_{298} = entropy of a mole of the compound, (cal/mol·K)

(g) = gas

(l) = liquid

(s) = solid (crystalline)

An asterisk (*) indicates values calculated by interpolation. Less reliable data are given in parentheses.

A. Inorganic Compounds

Substance	ΔH^0_{298}	ΔG^0_{298}	S^0_{298}
AgBr (s)	-23.78	-22.93	25.60
AgCl (s)	-30.362	-26.224	22.97
AgF (s)	-48.5	-44.2	20
$AgNO_3$ (s)	-29.43	-7.69	33.68
$AgCO_3$ (s)	-120.97	-104.48	40.0
Ag_2S (s)	-7.306	-2.586	29.09
Ag_2S (α)	-7.60	-9.62	34.8
Ag_2SO_4 (s)	-170.50	-147.17	47.8
$AlCl_3$ (s)	-166.2	-152.2	40.0
Al_2O_3 (α) (corundum)	-399.09	-376.77	12.186
$Al_2(SO_4)_3$	-820.98	-738.99	57.2
Al_2SiO_5 (s) (andalusite)	-642.2	-607.8	25.0
As_2O_3 (s)	-156.97	-137.68	25.6
As_2O_5 (s)	-218.6	-184.6	25.2
BCl_3 (g)	-94.5	-90.9	69.29
B_2O_3 (s)	-302.0	-283.0	12.91
$BaCl_2$ (s)	-205.56	-193.8	30
$BaCO_3$ (s)	-291.3	-272.2	26.8
BaO (s)	-133.4	-126.3	16.8
$BaSO_4$ (s)	-350.2	-323.4	31.6
BeO	-146.0	-139.0	3.37

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Substance	ΔH^0_{298}	ΔG^0_{298}	S^0_{298}
$BiCl_3$ (s)	-90.61	-76.23	45.3
Bi_2O_3 (s)	-137.9	-118.7	36.2
Bi_2S_3 (s)	-43.8	-39.4	35.3
CCl_4 (g)	-25.5	-15.3	73.05
CO (g)	-26.416	-32.808	47.301
CO_2 (g)	-94.052	-94.260	51.061
$COCl_2$ (g)	-53.30	-50.31	69.13
COS (g)	-32.80	-40.45	55.34
CS_2 (g)	27.55	15.55	56.84
CaC_2 (α)	-15.0	-16.2	16.8
$CaCO_3$ (s)	-288.45	-269.78	22.2
$CaCl_2$ (s)	-190.0	-179.3	27.2
CaO (s)	-151.9	-144.4	9.5
$Ca(OH)_2$ (s)	-235.80	-214.33	18.2
CaS (s)	-115.3	-114.1	13.5
$CaSO_4$ (s)	-342.42	-315.56	25.5
$CaSO_4 \cdot 2H_2O$ (s)	-483.06	-429.19	46.36
$CaSiO_3$ (s)	-378.6	-358.2	19.6
$CdCO_3$ (s)	-178.7	-160.2	25.2
$CdCl_2$ (s)	-93.00	-81.88	28.3
CdO (s)	-60.86	-53.79	13.1
CdS (s)	-34.5	-33.6	17
$CdSO_4$ (s)	-221.36	-195.99	32.8
ClO_3 (g)	24.7	29.5	59.6
Cl_2O (g)	18.20	22.40	63.70
$CoCl_2$ (s)	-77.8	-67.5	25.4
$CoSO_4$ (s)	-207.5	-182.1	27.1
Cr_2O_3 (s)	-269.7	-250.2	19.4
Cr_4C (s)	-16.4	-16.8	25.3
CuCl (s)	-32.2	-28.4	21.9
CuO (s)	-37.1	-30.4	10.4
Cu_2O (s)	-39.84	-34.98	24.1
CuS (s)	-11.6	-11.7	15.9
Cu_2S (s)	-19.0	-20.6	28.9
$CuSO_4$ (s)	-184.00	-158.2	27.1
$CuSO_4 \cdot 5H_2O$ (s)	-544.45	-449.3	73.0
D_2O (g)	-59.563	-56.067	47.379
D_2O (l)	-70.413	-58.206	18.162
F_2O (g)	5.5	9.7	58.95
$FeCO_3$ (s)	-178.70	-161.06	22.2
$FeCl_2$ (s)	-81.5	-72.2	28.6
FeO (s)	-63.7	-58.4	12.9
Fe_2O_3 (s)	-196.5	-177.1	21.5
Fe_2SiO_4 (s)	-343.7	-319.8	35.4

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Substance	ΔH^0_{298}	ΔG^0_{298}	S^0_{298}
Fe_3C (α) (cementite)	5.0	3.5	25.7
Fe_3O_4 (s)	-267.0	-242.4	35.0
Ga_2O_3 (s)	-258.0	-	-
$GeCl_4$ (l)	-130.0	-	-
GeO (s)	-22.8	28.2	52.56
H (g)	52.089	48.57	27.393
HBr (g)	-8.66	-12.72	47.437
HCN (g)	-31.2	28.7	48.23
HCl (g)	-22.063	-22.769	44.617
HF (g)	-64.2	-64.7	41.47
HJ (g)	6.20	0.31	49.314
HNO_3 (l)	-41.40	-19.1	37.19
H_2O (g)	-57.789	-54.634	45.106
H_2O (l)	-68.317	-56.690	16.716
H_2O_2 (l)	-44.84	(-28.1)	25.3
H_2S (g)	-4.815	-7.892	49.15
H_2SO_4 (l)	(193.91)	(-164.3)	37.50
$HgCl_2$ (s)	-53.4	-42.4	34.5
HgO (s, cr)	-21.68	-13.99	17.2
HgS (s, cr)	-13.90	-11.67	18.6
Hg_2Cl_2 (s)	-63.32	-50.35	46.2
InCl (s)	-44.5	-	-
$InCl_3$ (s)	-128.4	-	-
InO (s)	-222.5	-	-
$Kal(SO_4)_2$ (s)	-589.24	-534.29	78.9
KBr (s)	-93.73	-90.63	23.05
KCl (s)	-104.175	-97.592	19.76
$KClO_3$ (s)	-93.50	-69.29	34.17
KF (s)	-134.46	-127.42	15.91
$KMnO_4$ (s)	-194.4	-170.6	41.03
KNO_3 (s)	-117.76	-93.96	31.77
K_2SO_4 (s)	-342.66	-314.62	42.0
LiCl (s)	-97.70	-91.8*	13*
$LiNO_3$ (s)	-115.28	-91.7*	17*
Li_2CO_3 (s)	-290.54	-270.66	21.60
$MgCl_2$ (s)	-153.40	-141.57	21.4
$Mg(NO_3)_2$ (s)	-188.72	-140.63	39.2
MgO (s)	-143.84	-136.13	6.4
$Mg(OH)_2$ (s)	-221.0	-199.27	15.09
$MgSO_4$ (s)	-305.5	-280.5	21.9
$MgSiO_3$ (s)	-357.9	-337.2	16.2
$MgCl_2$ (s)	-115.3	-105.5	28.0

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Substance	ΔH^0_{298}	ΔG^0_{298}	S^0_{298}
MnO (s)	-92.0	-86.8	14.4
MnO_2 (s)	-124.5	-111.4	12.7
MnS (s)	-48.8	-49.9	18.7
$MnSO_4$ (s)	-245.24	-228.48	26.8
MoO_3 (s)	-180.33	-161.95	18.68
MoS_2 (s)	-55.5	-53.8	15.1
NH_3 (g)	-11.04	-3.976	46.01
NH_4Cl (s)	-75.38	-48.73	22.6
$(NH_4)_2SO_4$ (s)	-28.86	-215.19	52.65
NO (g)	21.60	20.719	50.339
NO_2 (g)	8.091	12.390	57.47
NOCl (g)	12.57	15.86	63.0
N_2O (g)	19.49	24.76	52.58
N_2O_4 (g)	2.309	23.491	72.73
N_2O_2 (g)	-0.6	(26)	82
NaBr (s)	-86.03	-83.5*	21.8*
NaCl (s)	-98.232	-91.785	17.30
NaJ (s)	-68.84	-68.2*	24.0
$NaNO_3$ (s)	-111.54	-87.45	27.8
NaOH (s)	-101.99	(-90.3)	15.34
Na_2CO_3 (s)	-270.3	-250.4	32.5
Na_2S (s)	-99.4	-90.0	17.4
$Na_2SO_4 \cdot 10H_2O$ (s)	-1033.8	-870.93	141.7
Na_2SiO_3 (s)	-363	-341	27.2
$NiCO_3$	-164.7*	-146.7	21.6*
$NiCl_2$	-75.5	-65.1	25.6
NiO (s)	-58.4	-51.7	9.22
NiS (s)	-18.6	-18.2*	-
$NiSO_4$(s)	-213.0	-184.9	18.6
O (g)	59.15	54.994	38.469
OH (g)	10.06	8.93	43.69
OsO_4 (g)	-91.7	-70.5	34.7
PCl_3 (g)	-73.22	-68.42	74.49
PCl_5 (g)	-95.35	-77.59	84.3
PH_3 (g)	2.21	4.36	50.2
$POCl_3$ (g)	-141.5	-130.3	77.59
$PbCl_2$ (s)	-85.85	-75.04	32.6
PbO (s) (yellow)	-52.07	-45.05	16.6
PbO (s) (red)	-52.40	-45.25	16.2
PbO_2 (s)	-66.12	-52.34	18.3
PbS (s)	-22.54	-22.15	21.8
$PbSO_4$ (s)	-219.50	-193.89	35.2
SO (g)	19.02	12.78	53.04

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Substance	ΔH^0_{298}	ΔG^0_{298}	S^0_{298}
SO_2 (g)	-70.96	-71.79	59.40
SO_3 (g)	-94.45	-88.52	61.24
$SbCl_3$ (s)	-91.34	-77.62	44.5
Sb_2O_5 (s)	-234.4	-200.5	29.9
Sb_2S_3 (s)	-35.7	-36.93	39
SiC (s)	-26.7	-26.1	6
$SiCl_4$ (g)	-145.7	-136.2	3.935
SiO_2 (s) (α-quartz)	-205.4	-192.4	79.2
SiO_2 (s) (α-cristobalite)	-205.0	-192.1	10.00
SiO_2 (glass)	-202.5	-190.9	10.19
$SnCl_4$ (l)	-130.3	-113.3	11.2
SnO (s)	-68.4	-61.5	61.8
SnO_2 (s)	-138.8	-124.2	13.5
SnS (s)	-18.6	-19.7	12.5
$SrCO_3$ (s)	-291.2	-271.9	23.6
$SrCl_2$ (s)	-198.0	-186.7	23.2
SrO (s)	-141.1	-133.8	28.13.0
TeO_2 (s)	-77.69	-64.60	16.99
$ThCl_4$ (s)	-285	-263.1*	46.8*
ThO_2	-292	272.5*	-
TiC (s)	-54	-53	5.8
$TiCl_4$ (g)	-	-	84.4
TiO_2 (s) (rutile)	-218	-203.8	12.01
UO_3 (s)	-302.84	-283	23.57
UCl_4 (s)	-251.2	-230.0	47.4
UO_2 (s)	-270	257	18.6
$UO_2(NO_3)_2$ (s)	-329.2	-273.1	66
V_2O_3 (s)	290	-271	23.58
$ZnCO_3$ (s)	-194.2	-174.5	19.7
$ZnCl_2$ (s)	-99.40	-88.255	25.9
ZnO (s)	-83.17	-76.05	10.5
ZnS (s)	-48.5	-47.4	13.8
$ZnSO_4$ (s)	-233.88	-208.31	29.8
$ZrCl_4$(s)	-230	-209	44.5
ZrO_2 (s)	-258.2	-244.4	12.03

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B. Organic Compounds

Formula and name of substance	ΔH^0_{298}	ΔG^0_{298}	S^0_{298}
CH_4 (g), methane	-17.889	-12.140	-44.50
C_2H_2 (g), acetylene	54.194	50.000	47.997
C_2H_4 (g), ethylene	12.496	16.282	52.45
C_2H_6 (g), ethane	-20.236	-7.860	54.85
C_3H_4 (g), methyl acetylene	44.319	46.313	59.30
C_3H_4 (g), propadiene	45.92	48.37	58.30
C_3H_6 (g), cyclopropane	16.89	24.940	56.81
C_3H_6 (g), propylene	4.879	14.990	63.80
C_3H_8 (g), propane	-24.820	-5.614	64.51
C_4H_6 (g), 1, 3-butadiene	26.33	36.01	66.62
C_4H_6 (g), dimethyl acetylene	34.97	44.32	67.71
C_4H_6 (g), 1-butylene	-0.03	17.09	73.04
C_4H_8 (g), cis-2-butylene	-1.67	15.74	71.90
C_4H_8 (g), trans-2-butylene	-2.67	15.05	70.86
C_4H_8 (g), 2-methyl propylene	-4.04	13.88	70.17
C_4H_{10} (g), *n*-butane	-30.15	-4.10	74.12
C_4H_{10} (g), isobutene	-32.15	-5.00	70.42
C_5H_{12} (g), 2-methyl butane	-36.92	3.50	82.12
C_5H_{12} (g), 2,2-dimethyl propane	-39.67	-3.64	72.23
C_5H_{12} (g), *n*-pentane	-35.00	-2.00	83.40
C_6H_6 (g), benzene	11.718	29.756	41.30
C_6H_6 (l), benzene	19.820	30.989	64.34
C_6H_{12} (g), cyclohexane	-29.43	7.59	71.28
C_6H_{12} (l), ditto	-37.34	6.37	48.85
C_6H_{14} (g), *n*-hexane	-39.96	0.07	92.83
C_7H_8 (g), toluene	11.950	29.228	76.42
C_7H_8 (l), ditto	2.867	27.282	52.48
C_7H_{16} (g), *n*-heptane	-44.89	1.94	102.24
C_8H_8 (g), styrene	35.22	51.10	82.48
C_8H_{10} (l), ethyl benzene	-2.977	28.614	60.99
C_8H_{10} (g), 1,2-dymethyl benzene (*o*-xylene)	4.540	29.177	84.31
C_8H_{10} (l), ditto	-5.841	26.370	58.91
C_8H_{10} (g), 1,3-dymethyl benzene (*m*-xylene)	4.120	28.405	85.49
C_8H_{10} (l), ditto	-6.075	25.730	60.27
C_8H_{10} (g), 1,2-dymethyl benzene (*n*-xylene)	4.290	28.952	84.23
C_8H_{10} (l), ditto	-5.838	26.310	59.12
C_8H_{18} (g), *n*-octane	-49.82	3.95	111.55
$C_{10}H_8$ (s), naphthalene	18.75	48.10	40.01
$C_{12}H_{10}$ (s), diphenil	24.53	61.26	49.2
$C_{14}H_{10}$ (s), anthracene	25.53	62.95	49.6
$C_{14}H_{10}$ (s), phenanthrene	26.65	63.77	50.6
CH_4O (g), methyl alcohol	-48.08	38.69	56.8
CH_4O (l), ditto	-57.02	-39.73	30.3
C_2H_6O (g), ethyl alcohol	-56.24	-40.30	67.4

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Formula and name of substance	ΔH^0_{298}	ΔG^0_{298}	S^0_{298}
C_2H_6O (l), ditto	-66.356	-41.77	38.4
C_3H_8O (g), propyl alcohol	-62.228	-39.115	75.9
C_3H_8O (g), isopropyl alcohol	-65.328	-41.913	73.2
$C_4H_{10}O$ (g), ethyl ether	-45.60	-28.1	
C_4H_{10} (l), ditto	-65.3	-27.88	60.5
CH_2O (g), formaldehyde	27.7	-26.3	52.26
C_2H_4O (g), acetaldehyde	-39.76	-31.96	63.5
C_3H_6O (g), acetone	-51.72	-36.3	70.49
CH_2O_2 (g), formic acid	-86.67	-80.24	60.0
CH_2O_2 (l), ditto	-97.8	-82.7	30.82
$C_2H_4O_2$ (s), acetic acid	-104.3	-91.2	70.1
$C_2H_4O_2$ (l), ditto	-116.4	-93.8	38.2
$C_2H_2O_4$ (s), oxalic acid	-197.6	-166.8	28.7
$C_7H_6O_2$ (s), benzoic acid	-91.91	-58.5	40.04
$CHCl_3$ (g), chloroform	-24	-16	70.86
$CHBr_3$ (g), bromoform	6	3.8	79.18
CH_2Cl_2 (g), dichloromethane	-21	-14	64.68
CH_2Br_2 (g), dibromomethane	-1	-1.4	70.16
CH_3F (g), methyl fluoride			53.30
CH_3Cl (g), methyl chloride	-19.6	-14.0	55.97
CH_3Br (g), methyl bromide	-8.5	-6.2	58.74
CH_3I (g), methyl iodide	4.9	5.3	60.85
CH_4ON_2 (s), carbamide (urea)	-79.634	-47.12	25.00
C_2H_5Cl (g), ethyl chloride	-25.1	-12.7	65.90
C_6H_7N (l), aniline	8.44	36.62	45.8
$C_6H_5NO_2$ (l), nitrobenzene	3.80	34.95	53.6

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TABLE 2. Energy of Chemical Bonds

Bond	Molecule	Bond energy, (Kcal/mol)	Bond	Molecule	Bond energy, (Kcal/mol)
C – H	Alkanes	98.7	C ≡ N	HCN; $(CN)_2$	207.9
C – H	Alkenes	99.4	O – H	H_2O	109.4
C – H	Alkynes HCN, $CHCl_3$	96.3	O – H	Alcohols	104.7
			O – F	F_2O	45.0
C – H	Benene	100.7	O – Cl	Cl_2O	48.9
C – Cl	Alkyl chlorides	76.0	O – O	H_2O_2	33.3
C – Cl	CCl_4 and $CHCl_3$	75.8	S – H	H_2S	86.8
C – Cl	$COCl_2$	74.4	S – Cl	S_2Cl_2	71.0
C – Br	Alkyl bromides	63.3	S = O	SO_2	125.9
C – I	Alkyl iodides	47.2	S – S	S_2Cl_2	69.0
C – C	Alkanes $(CN)_2$	79.3	N – H	NH_3, amines	92.0
C – C	RCHO; RR'CO	83.8	N = O	Nitroalkanes	103.9
C – C	Benzene ring	116.4	N ≡ O	NO	149.4
C = C	Alkenes	140.5	N – N	N_2O_4	42.5
C ≡ C	Alkynes	196.7	As – H	AsH_3	47.5
C – O	Alcohols, ethers	79.6	As – Cl	$AsCl_3$	60.3
C = O	RCHO; RR'CO	168.7	As – Br	$AsBr_3$	51.8
C = O	CO_2	191.0	As – I	AsI_3	33.1
C ≡ O	CO	255.8	As – As	As_4	15.1
C – N	Amines, nitro-alkanes	65.9			

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TABLE 3. Standard States for Thermodymanic Calculations[a]

Physical State	Chemical Potential	Enthalpy[b]	Entrpy	Volume
Pure gas	Hypotetical ideal gas at 1 bar (0.1 Mpa). There also will be a pressure, usually near 1 bar, at which the real gas has a fugacity of unity	Hypotetical ideal gas at 1 bar; also real gas at zero pressure (see Exercise 1, this chapter)	Hypotetical ideal gas at 1 bar (0.1 Mpa). There also will be a pressure of the real gas, not zero and that of unit fugacity, with an entropy equal to that in the standard state	Hypotetical ideal gas at 1 bar (0.1 Mpa). $V_m^o = RT / P^o$
Pure liquid or pure solid	1 bar (0.1 MPa)	1 bar (0.1 MPa)	1 bar (0.1 MPa)	1 bar (0.1 MPa)
Solvent in a solution[c]	Pure solvent at vapor pressure of pure solvent	Pure solvent at vapor pressure of pure solvent	Pure solvent at vapor pressure of pure solvent	Pure solvent at vapor pressure of pure solvent
Solute in a solution[c,d]	Hypotetical 1-molal solution obeying limiting low corresponding to Henry's law at vapor pressure of pure solvent. There also may be a finite concentration, not equal to zero, at which the activity of the solute is unity. This may be considered as the standard state *only in free energy* calculations	Hypotetical 1-molal solution obeying limiting low corresponding to Henry's law at vapor pressure of pure solvent. The value of partial molar enthalpy in the standard state, H_{m2}^o, is always equal to that at infinite dilution. Hence, the *infinitely dilute solution* can be considered *the standard state only in enthalpy calculations*	Hypotetical 1-molal solution obeying limiting low corresponding to Henry's law at vapor pressure of pure solvent. There also may be a solution of finite concentration, not equal to zero but also not having an activity of unity, with partial molar entropy of solute equal to that in standard state	Hypotetical 1-molal solution obeying limiting low corresponding to Henry's law at vapor pressure of pure solvent. The value of V_{m2}^o is equal to V_{m2}^∞

[a] For every case it is assume that the temperature has been specified.

[b] The standard state for the heat capacity is the same as that for the enthalpy.

[c] this choice of standard state for components of a solution is different from that used by many thermodynamicists. It seems preferable to the choice of a 1-bar standard state, however, because it is more consistent with the extrapolation procedure by which the standard state is

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determined experimentally, and it leads to a value of the activity coefficient equal to 1 when the solution is ideal or very dilute whatever the pressure. It is preferable to a choice of the pressure of the solution, because that choice produces a different standard state for each solution.

[d] A more elegant (though more difficult to visualize) formulation of the procedure for the selection of the standard state for a solute may be made as follows: From Equation

$$\mu_2 = \mu_2^o + RT \ln a_2$$

and from Equation

$$a_2 = \frac{m_2 \gamma_2}{m_2^o}$$

it follows that

$$\mu_2^o = \mu_2 - RT \ln \frac{m_2}{m_2^o} - RT \ln \gamma_2$$

Therefore the state in which the solute has a partial molar free energy of μ_2^o can be found from the following limit, since γ_2 approaches unity as m_2 approaches zero.

$$\lim_{m_2 \to 0} \left(\mu_2 - RT \ln \frac{m_2}{m_2^o} \right) = \mu_2^o$$

With this method of formulation it also is possible to show that frequently there is a real solution at some molality $m_{2,I}$ for which $\mu_2 = \mu_2^o$, that H_{m2}^o corresponds to H_{m2} for a real solution at infinite dilution, and that S_{m2}^o equals S_{m2} for a real solution at a molality $m_{2,k}$, which is neither zero nor $m_{2,J}$.

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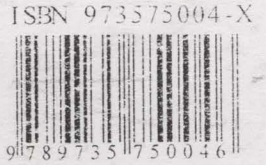

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